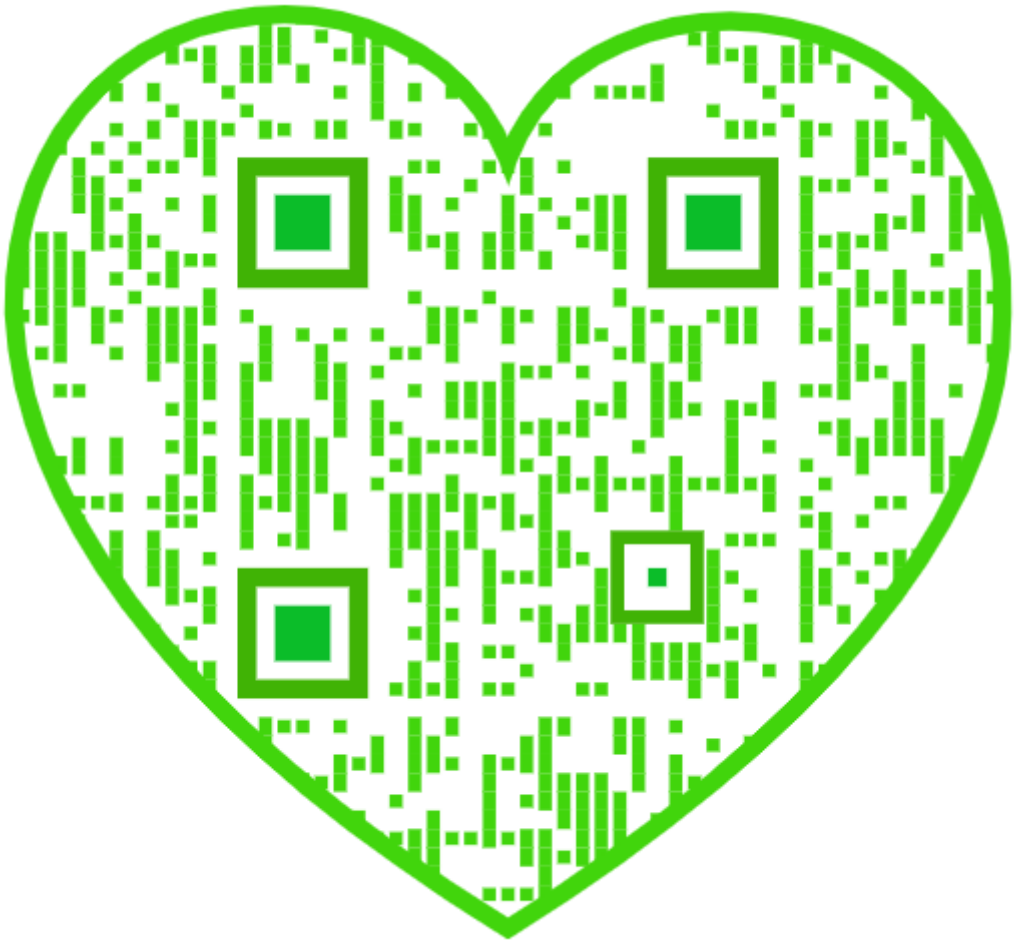

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# BONE PRODUCTS AND MANURES

*An Account of the Most Recent Improvements in the Manufacture of Fat, Glue, Animal Charcoal, Size, Gelatine, and Manures*

BY

THOMAS LAMBERT

TECHNICAL AND CONSULTINO CHEMIST

ILLUSTRATED BY TWENTY PLANS AND DIAGRAMS

LONDON

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# PREFACE

In the present volume, the author has endeavoured to place before manufacturers, students of technology, and others interested, a practical and comprehensive account of the modern method of fat extraction and the manufacture of glue, size, gelatine, manures, etc.

This branch of industry is undergoing a great change. Old and wasteful methods of working are giving way to newer processes, based on the teachings of chemical science, and which self-interest compels the manufacturer to adopt. The book is arranged in nine chapters, and is fully illustrated with drawings of the most modern type of plant.

To enhance the value of the work, the author has devoted a chapter exclusively to the methods used in making the many analyses of raw and finished products, and which, he believes, will be of service to chemists engaged in this class of work.

The illustrations have been specially drawn for the work by Mr. Levi Lambert, to whom I must express my obligations.

THOMAS LAMBERT

Wigan, *March* 1901.

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# BONE PRODUCTS AND MANURES

## PART I.—BONE PRODUCTS.

### CHAPTER I.

#### The Treatment of Bones.

Chemically speaking, the framework supporting the fleshy tissues of the animal order, and which we call bone, is a combination of phosphates of lime and magnesia, carbonate of lime, and alkaline salts, united with fatty and cartilaginous matter. To the latter we look for our yield of glue; to the fatty matter for the fat contained, and to the phosphates for the basis of our manure trade.

Bone cartilage is composed of carbon, hydrogen, oxygen, and nitrogen. The percentage composition is practically constant, whether the cartilage be from an old or young animal, as is seen from the following analyses by Fremy:—

| Cartilage from | Carbon. | Hydrogen. | Nitrogen. | Oxygen. |
|---|---|---|---|---|
| Ox, old . . | 49·81 % | 7·14 % | 17·32 % | 25·67 % |
| Calf . . | 49·9 % | 7·3 % | 17·2 % | 25·6 % |

The bones of the young are, however, much richer in cartilage than those of the old. This is reversed in the case of the inorganic or mineral matter, the old having the greatest yield of phosphates.

Then again, the fatty matters are more in evidence in full-grown animals than in youth or age; also in the thigh and leg bones the yield is higher than in the heads, ribs, or

shoulder-blades, the latter averaging 12 to 13 per cent., whilst the former runs 18 to 19 per cent.

To separate the different classes of bone coming into a work, and range them according to the amounts they would produce of fat and glue, may be a desirable object, but in practice it is not carried out. The manufacturer would have tedious work in front of him in separating, say, the bones of sheep, calves, oxen, horses, or pigs, and subdividing these again into heads, ribs, breasts, shoulders, feet, etc. Bones are mainly bought by contract from various dealers in the towns within easy railway access to the works. The rates are generally fixed for twelve months, and cover all classes of common bones, whether fresh butchers' or a mixture with partly boiled bones. The only discrimination is made with the marrows, which are bagged separately, and bring as much as 6s. 6d. per cwt. Bones differ considerably in their value. A fresh bone will yield the highest percentage of fat and glue. On the other hand, the writer has found only 6 per cent. fat with 30 per cent. water in partly boiled bones. The dealer sometimes finds ways and means of including hoofs, horns, iron, beefy matter, and even pieces of brick. Naturally they form weight, but, excepting the horns, have no value. With careful sorting, this adulterant is detected, and a reduction in the weight charged for is made accordingly. The manufacturer, as a rule, is open to treat for material from all sources: it may be the putrid ham or bacon from the provision merchant's store, diseased fatty meat condemned by a zealous inspector, and even infected pigs, slaughtered by official order, are brought at times to the mouth of the benzene extractor; also the writer has seen a cargo of cotton seed, damaged by water, treated for the oil by the benzene process.

The arrangement and situation of a bone factory is a matter of great importance. The works should have easy access to main lines of railway, with ample siding accom-

modation; a canal connection would also be of advantage. A plentiful supply of water and a good outflow for all effluents are a necessity. In fixing the site, choose a position outside the boundaries of a town, so that the offensive smell which arises from all works of this character should not be made a matter of complaint by a populous community. The lighting of the works is another consideration. Probably the district has no gas connection with a town; it would then be advisable to fit up a complete electric installation, lighting, say, 140 to 150 lamps. On the other hand, if the manufacturer carbonises the bones for the making of "char," then he has at hand a large volume of uncondensable gases of high illuminating power, which, after purification, are stored in a gasometer, for ultimate use in lighting the works and for motive power in driving machinery.

In arranging the works, the benzene house, with its storage accommodation for benzene, should be a building apart from the main buildings, and the crushed bones carried by an elevator to the charging floor. The plant should be arranged so that the different processes can be carried through with a minimum of labour and quick transition between each, and every facility for loading the finished goods.

The raw bones, which at times are very heavily surcharged with moisture, should not be allowed to accumulate for any unreasonable time, as they begin to smell heavily; the cartilage turns black from decomposition, which means a loss in the ultimate yield of glue. The first operation is the sorting; the bones are thrown on to a table, from which is fed a crusher or "cracker." Here several women are constantly engaged separating the rags, iron, beefy matter, hoofs, horns, etc. As they are sorted the bones are pushed to the mouth of the crusher, thence falling on to fixed and revolving steel "cutters," breaking them into pieces three to four inches long. This enables the benzene in the after process

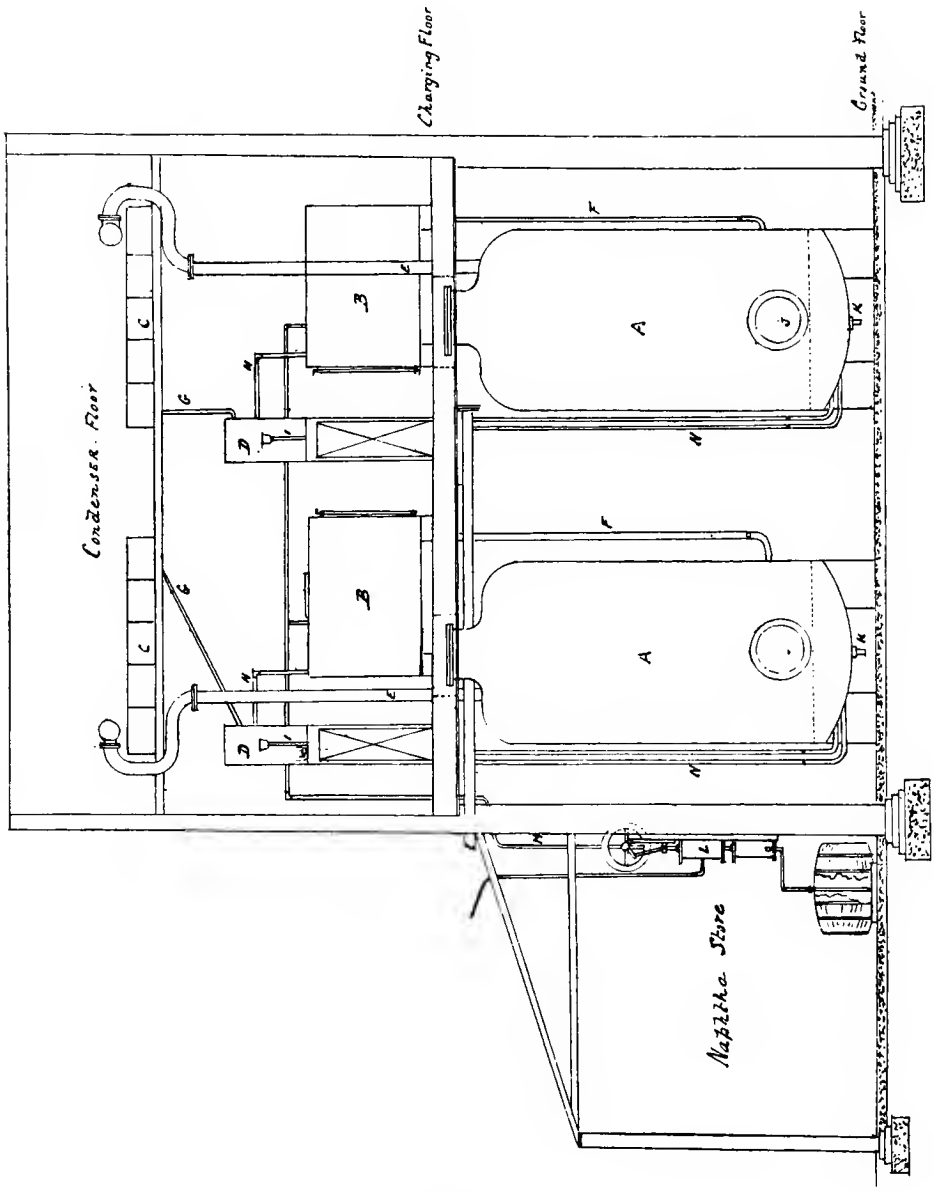

Charging Floor
Ground Floor
Condenser Floor
A
B
C
D
E
F
G
H
K
L
N
Naphtha Fire

FIG. 1.

to get right to the centre of the bone. Falling on to an elevator, the crushed bone is carried to the charging floor of the benzene house.

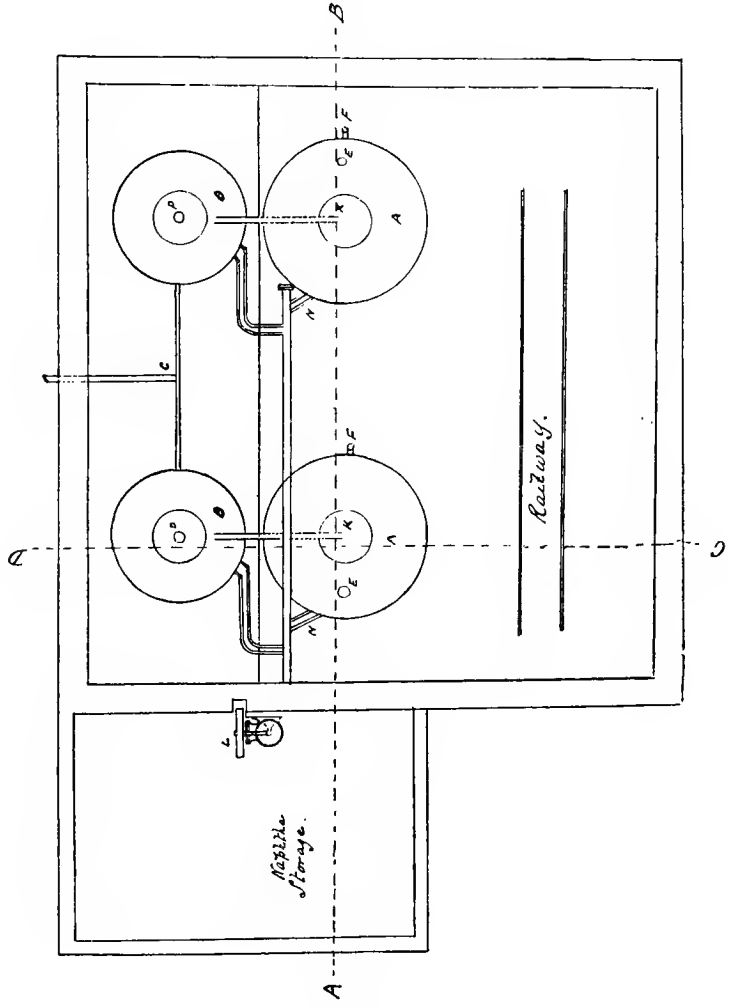



FIG. 2.

In Figs. 1, 2, and 3 the most modern system of degreasing is shown in longitudinal section, plan, and section

respectively. The house is what is termed a "100-ton

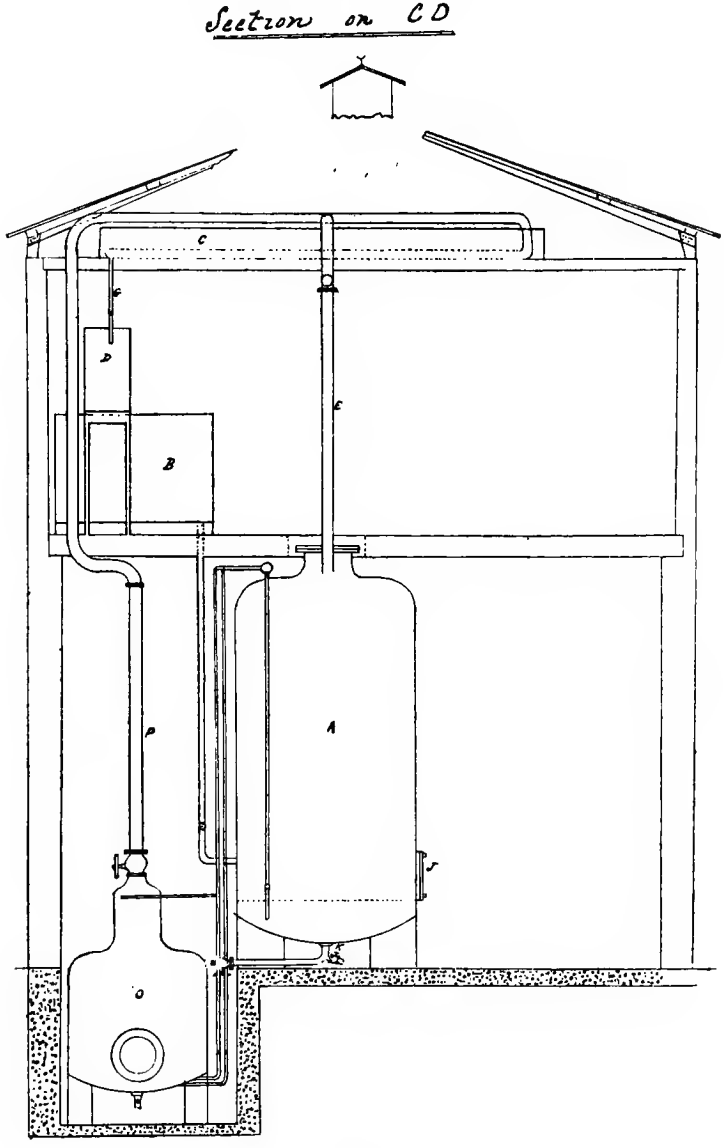



FIG. 3.

house,"—that is, the plant is capable of degreasing 100 tons of bones in five working charges. *AA* are the two extractors, holding about ten tons each. They are built of the best mild steel, and fitted with perforated false bottoms, underneath which rest the dry and wet steam coils supplied by *NN*. Each has a manhole at *JJ*, through which the extractors are emptied, the degreased bones being carried away to another part of the works by the "bogey" railway, as seen in the plan. Both extractors have inlet naphtha pipes *FF*, which are fed from the two large storage tanks *BB*. The outlet pipes for the naphtha vapours are at *EE*, the vapours thence passing into the condensers *CC*. Each condenser is divided into five divisions, each connected so that the circulation of water is complete over the whole. The inlet pipes to the condensers are 6-in. diameter, and this bore is gradually reduced to $2\frac{1}{2}$-in. diameter in the outlet pipes *GG*, which carry the condensed naphtha and water to the Florentine receivers or separators *DD*. Here, from their own gravities, the separation between the two liquids is instantaneous, the water leaving by the pipes *II*, the naphtha passing through *HH* to the storage tank, to be passed again over the charge in the extractors.

The naphtha store is shown at the end of the building, and contains the pumping-engine *L*, which lifts the naphtha from the barrels, through the pipe *M*, and on to the storage tanks.

In section and plan is seen the position of the mont-jus or distiller, into which is run the fat from the extractor at *K*. The fat retains a fair proportion of naphtha, and the work of the mont-jus is to distil this over, the vapours passing through the pipe *P*, and entering the condenser *C*. The fat is then blown up by steam to an outside vat, and flows from thence to the clarifying vats in the main buildings of the works.

The quality of benzene used is a matter of serious import

to the manufacturer. The term "benzene" is a general one, and applies to either American or Russian petroleums, Scotch shale oils, solvent naphthas, etc. The value for extractive purposes of a "benzene" is based on the boiling-point and what distils over between certain temperatures. If a benzene be used with a low boiling-point, and with a large percentage distilling over under the boiling-point of water (212° F.), then the action in the extractor becomes too rapid, the benzene being distilled over before it has time to do its work as a solvent, consequently the bones after treatment remain moist, and retain probably 3 to 4 per cent. of fat. On the other hand, if a benzene be used with a high boiling-point, and a large proportion fractionating over above 270° F., then the operation takes longer in the extractor, a heavier steam pressure is necessary to drive over the heavy hydrocarbons of the oil, which may not come over before a temperature of 330° to 340° F. is reached. This prolonged and high steam pressure will attack the cartilaginous matter of the bone, and thus lessen the quantity and injure the quality of the glue produced.

A good working benzene should boil at or about 212° F., with little or nothing coming over below that temperature, while at 270° F. 98 to 99 per cent. should distil over, leaving 1 to 2 per cent. to be driven off between 270° to 280° F.

The following four fractionations represent the differences in the value of naphthas for extraction purposes.

| No. 1. Boiling-point, 212° F. | |
|---|---|
| Below 212° F. | Nothing. |
| 212° to 220° F. | 14 per cent. |
| 220° to 230° F. | 20½ ,, |
| 230° to 240° F. | 38 ,, |
| 240° to 250° F. | 16½ ,, |
| 250° to 260° F. | 6 ,, |
| 260° to 270° F. | 4 ,, |
| 270° to 280° F. | 1 ,, |
| Over 280° F. | Nothing. |

No. 2. Boiling-point, 212° F.

| | |
|---|---|
| Below 212° F. | Nothing. |
| 212° to 220° F. | 6 per cent. |
| 220° to 230° F. | 31 „ |
| 230° to 240° F. | 40 „ |
| 240° to 250° F. | 20 „ |
| 250° to 260° F. | 2 „ |
| 260° to 270° F. | 1 „ |
| Over 270° F. | Nothing. |

No. 3. Boiling-point, 180° F.

| | |
|---|---|
| 180° to 192° F. | 63 per cent. |
| 192° to 212° F. | 26 „ |
| 212° to 230° F. | 8 „ |
| 230° to 260° F. | 3 „ |
| Over 260° F. | Nothing. |

No. 4. Boiling-point, 234° F.

| | |
|---|---|
| 200° to 234° F. | 8 per cent. |
| 234° to 250° F. | 22 „ |
| 250° to 260° F. | 18 „ |
| 260° to 270° F. | 15 „ |
| 270° to 280° F. | 12 „ |
| 280° to 290° F. | 9 „ |
| 290° to 300° F. | 5 „ |
| Over 300° F. | 11 „ |

In practical working of these naphthas, Nos. 1 and 2 would give the best results, leaving a dry, well degreased bone and the cartilage practically untouched.

No. 3 would leave the cartilage unattacked, but the bone will retain an appreciable amount of moisture and fat.

In No. 4, although the bone would be well degreased, the time of extraction would be longer than in Nos. 1 and 2, and with a greater steam pressure, which would injure the cartilage for subsequent glue-making.

A peculiar property possessed by benzene is that, if allowed to remain quiescent on bones for several hours, it has the power of dissolving not only the fat, but also attacking

and partly dissolving the cartilaginous matter; thus the plan of steeping the bones in the hydrocarbon for several hours, and then distilling over, produced a fat carrying with it a goodly portion of cartilaginous matter, which not only meant a loss, but was very difficult to separate in the after clarification of the fat. Improvements were made on this plan by American manufacturers adopting a plan of allowing the hydrocarbon to trickle through the mass. It is, however, to the German manufacturers that we are indebted for a perfected system of grease extraction, little of which is known in this country. So economical is the system in its working, that bones can be degreased leaving only ·2 to ·4 per cent. fat unextracted, and the loss of benzene on the tonnage of bones used is as low as ·4 per cent., which covers the benzene lost in working and that left in the crude fat. In eight different extractions with common bones and knuckle-ends, the latter holding 18 to 19 per cent. fat, the author only found—

| (1) | (2) | (3) |
|---|---|---|
| ·29 per cent. fat. | ·31 per cent. fat. | ·17 per cent. fat. |
| (4) | (5) | (6) |
| ·46 per cent. fat. | ·41 per cent. fat. | ·38 per cent. fat. |
| (7) | (8) | |
| ·50 per cent. fat. | ·27 per cent. fat. | |

In working the extractor, particular care is taken that each valve is open or shut as necessity demands, and the operation commences by allowing the benzene to flow from the storage tank to the extractor, until a depth of about twelve inches in the gauge-glass is reached. Meanwhile the steam is moderately turned on, which gradually warms the mass, and the distillation commences, as is seen by the thin stream of benzene and water running into the separator. The remaining benzene in the tank is now allowed to slowly flow into the extractor, and the volume of steam increased by

opening wider the valve. Gradually the flow of benzene and water from the condenser increases, and the separated naphtha rises in the storage tank. On taking the temperature at this point, a good indication is given whether the action is too rapid or too slow. When the distilled naphtha in the gauge-glass reaches a depth of 27 to 28 inches, the valves are closed, and the first run of fat is made to the mont-jus. A fresh charge of naphtha is then run into the extractor, and the naphtha feed-pipe kept a quarter open, so that the remaining portion from the storage tank shall trickle slowly into the mass of bones, the storage tank meanwhile being replenished by the distillation proceeding in the extractor. The naphtha, after condensation, leaving the extractor is greater than in entering, consequently the storage tank is again slowly filled. By these operations the naphtha is continually on the move and never quiescent. At the height of 27 to 28 inches the valves are closed, and the mont-jus receives its second supply of fat, which, as a matter of course, is less in quantity than the first run. The same operation is repeated a third time, forming the final charge, and the extracted fat, as before, is run to the mont-jus. The bones still retain a portion of the naphtha, along with some moisture, and to remove this and render the bones thoroughly dry, high-pressure steam is blown through the extractor until the very faintest of naphtha film only is noticed floating on the condenser liquor. This indicates that all the naphtha is practically driven over, and the operation may then be considered as finished. On completion, the manholes are opened, any steam allowed to escape, and the charge is then found in a thoroughly dried condition and ready for removal to the "bogey" railway. The weight yielded will be about 60 per cent. of the total weight of raw bones used.

As previously explained, the crude fat is run off at three different stages during the extraction, carrying with

it some 5 to 10 per cent. naphtha, along with water, fine phosphatic matter, and dirt from the bones. The steam is turned on the mont-jus and the fat boiled, the escaping naphtha passing through a 6-inch pipe to the condenser above. At the separator the workman carefully watches the decreasing flow of benzene, and when this practically ceases, the outlet valve is closed and steam injected to about 5 lb. pressure, which blows the fat through a 3-inch pipe to a large reserve tank placed outside the building. It may be said here that in boiling the fat in the mont-jus great care is necessary to prevent violent frothing, which would carry a portion of the fat up the outlet pipe to the condenser. To guard against this, a 1-inch perforated steampipe is fixed within the dome, and when the frothing commences it is kept under control by injecting a little steam through this spray pipe. This crude fat is tested daily for any benzene that it may contain. The benzene was as follows, in five samples drawn at different times :—

| | |
|---|---|
| 1st | ·15 per cent. benzene. |
| 2nd | ·17 ,, |
| 3rd | ·09 ,, |
| 4th | ·11 ,, |
| 5th | ·18 ,, |

A sample of the crude fat gave on analysis—

| | |
|---|---|
| Fat | 87·22 per cent. |
| Dirt | 4·86 ,, |
| Mineral matter | 3·67 ,, |
| Water | 4·12 ,, |
| Naphtha | ·13 ,, |

With proper caution and care in the working, the percentage of benzene left in the crude fat, which in the after process of clarification is lost, should not exceed the above results. To refine this crude product, a further boiling with steam and water is necessary, and is carried out in open

vats, the impurities allowed to subside, and the clear fat then run into casks for the market. The yield averages about 12¾ per cent. on the raw bones used. Bone fat thus produced is darker in colour than that made by boiling or steaming the bones, and some retain a very faint naphtha smell. In the after process of bleaching this is entirely got rid of, and the colour brought up to a good creamy white. However, to the stearine and glycerine manufacturers colour is no object, and it is sold to them unbleached. The stearine maker buys according to its "titer" and impurities, but more especially the latter, which is limited to 2 per cent. These impurities are given in the following four analyses of fat:—

| | (1) | (2) | (3) | (4) |
|---|---|---|---|---|
| Moisture . . | 1·38 % | 1·03 % | ·84 % | 1·40 % |
| Naphtha . . | ·06 % | ·13 % | ·08 % | ·07 % |
| Organic matter other than fat | ·09 % | ·27 % | ·63 % | ·18 % |
| Mineral matter, Ash, . . | ·16 % | ·19 % | ·41 % | ·15 % |
| "Titer" . . | 31·14 % | 33·85 % | 37·11 % | 32·05 % |

For the bleaching of fat several methods have been suggested, amongst which may be mentioned the action of air driven in finely divided streams through the fat heated to 190° to 200° F., as advocated by Dunn. Another process consists of the use of chlorate of potash in the proportion of ·2 per cent. of the fat used, with the addition of a small quantity of sulphuric acid. The use of "permanganate" finds favour as a bleaching agent, the fat being heated to about 200° F., and the "permanganate" dissolved in a little water, added along with sufficient dilute sulphuric acid to render the whole slightly acid. After heating for two hours water is added, and the liquor boiled. This is re-

peated several times, until the wash water is free from the "permanganate" tint.

On a simple chemical reaction depends the well-known bichromate method of Watts. Water glass has also been suggested for clarifying and bleaching of fats. To 1 ton of the fat brought to the boil one-fourth its weight of water is added, 40 lb. of sodium silicate (water glass) at 50° T., and 10 lb. bicarbonate of soda. During the boiling, the dirty matter comes to the surface, and is removed by

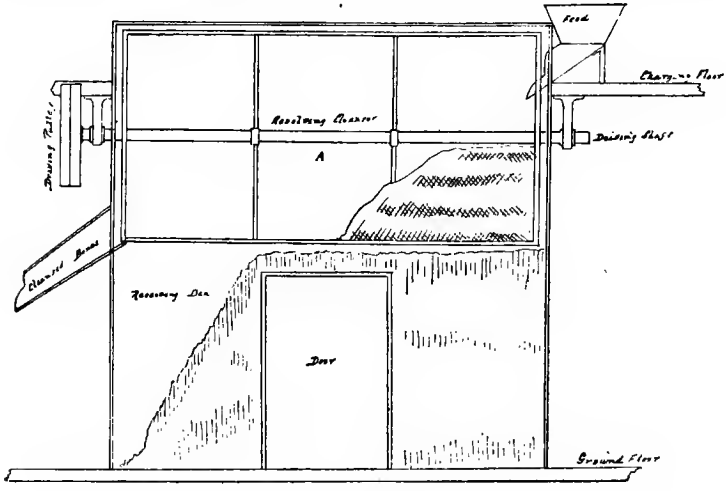



FIG. 4.

skimming. When the froth appears white the boiling is stopped, cold water added, and the whole allowed to rest for forty-eight hours. The fat is then removed to another vat, boiled with a fresh quantity of water, allowed to settle, and the clear fat run into coolers.

The degreased bones leaving the benzene house are carried by the railway to the mechanical cleanser. In Fig. 4 a longitudinal section is shown, with the receiving den underneath. The cleanser is a large cylindrical drum open at both ends, and covered with a strong 10-mesh wire

netting. The bones are lifted by a bucket elevator, falling into a hopper which feeds the cleanser, and are carried by the revolving motion to the other end, whence they fall into a "shute." In the den below falls the coarse meal passing through the netting. Four samples of this meal drawn at different times gave—

| | Equivalent to Tribasic Phosphate of Lime. | Nitrogen. |
|---|---|---|
| (1) | 30·25 per cent. | 6·22 per cent. |
| (2) | 26·18 „ | 4·79 „ |
| (3) | 32·37 „ | 5·85 „ |
| (4) | 29·15 „ | 5·12 „ |

The whole of the nitrogen is not glue-forming,—that is, it is not solely derived from the cartilaginous matter; a considerable portion has its origin in the hairy matter of skins, etc., which are connected to the bone, or pass loosely into the extractor. Still the meal retains an excess of nitrogen, which could more profitably be converted into glue than sold for the price of bone meal. The weight yielded averages 14 per cent. on the bones used. To save this excess of nitrogen, the coarse meal is passed through a smaller revolving cleanser, covered with a 30-mesh netting. Here fully half the weight is separated, and as it leaves the end of the cleanser is bagged and passed on to the glue-house for further treatment. The fine dust or flour passing through the 30-mesh is sold, or is used in the manure department of the works. Three samples of the fine flour gave—

| | (1) | (2) | (3) |
|---|---|---|---|
| Equivalent to tribasic phosphate of lime | 24·35 % | 26·29 % | 23·44 % |
| Nitrogen . . . | 1·67 % | 1·14 % | 1·07 % |

The gain in a second cleansing is seen in the considerable diminution of the nitrogen, which ultimately means an increase in the weight of glue yielded.

### Animal Charcoal.

The degreased and cleansed bones are either used by the manufacturer for making glue only, with boiled bones as a bye-product, for further conversion into superphosphates, or he may convert them direct into charcoal, with the subsidiary products of pitch, sulphate of ammonia, etc. A third course is open to him, and that is, he may partly degelatinise the bones, extracting 10 per cent. of the carbonaceous and nitrogenous matter as glue, and carbonise the remainder for charcoal. This procedure gives a lower yield of tar and ammoniacal products. It has been urged that the "char" yielded by this method is much inferior to that produced by carbonising the bone direct. No sufficient evidence has, however, been furnished to support the objection. On the other hand, from tests made of the decolorising power, carbon, and specific gravity, the quality is found fully equal to that of a "direct" made charcoal. Whether the bone has been partly degelatinised or retains the whole of the organic matter makes no difference in the process of manufacturing. When a bone is burnt or carbonised out of contact with air, it undergoes a great change, losing 38 to 40 per cent. of its weight, emitting empyreumatic, tarry, and ammoniacal vapours, and leaving a black mass, retaining the shape of the original bone. This mass, when milled, forms the granular body called "char." The products of distillation are classified into—

(1) Ammoniacal Liquor.
(2) Tar.
(3) Illuminating and other Gases.
(4) Char.

The yields vary according to the quality of bone burnt, and whether it has undergone a partial degelatinisation previously. Taking an average of good quality bones, 100 tons would give—

| | | |
|---|---|---|
| Char . . . . . | 61 | tons. |
| Ammoniacal liquor . . . | 13 | ,, |
| Tar . . . . . | 6 | ,, |
| Illuminating and other gases . | 20 | ,, |

The ammoniacal liquor consists of carbonate, hydrate, sulphide, chloride, and sulpho-cyanide of ammonia. The tar, on further distillation, yields bone pitch and oil, and from the latter have been fractionated pyridin, lutiden, aniline, phenol, and other complex bases, which up to the present have had no commercial value, however interesting they may be from a scientific standpoint.

The formation of these different bodies are the results of a very complicated series of chemical changes in the retort. Bone, as previously explained, is a combination of organic with mineral matter, in which phosphate of lime largely predominates. The mineral portion undergoes no change at the red heat of the furnace, excepting the reduction of the small quantity of sulphate of lime present to sulphide, and its subsequent conversion partly to sulphuretted hydrogen and partly to sulphurous acid. On the other hand, the organic matter breaks up—the hydrogen, oxygen, carbon, and nitrogen, of which it is composed, assume other combinations.

Part of the carbon is left with the mineral matter to form the char, and it is to the presence of this fixed carbon in a certain proportion that the char owes its valuable decolorising power. Another portion of the carbon goes to build up the various constituents forming the illuminating gases. A further portion is used in the formation of the oxides of carbon ($CO_2$ and $CO$); and lastly, a small portion unites with its combining equivalent of nitrogen to form the cyanogen present.

The whole of the nitrogen, excepting the small part used in the formation of cyanogen, forms, in the first instance, gaseous ammonia.

As the gases leave the retort, their temperature falls considerably, allowing a further grouping to come into play. The whole of the carbonic acid ($CO_2$) unites with its equivalent of ammonia, forming carbonate of ammonia, which is the principal ammoniacal compound in the liquor. The cyanogen and sulphuretted hydrogen take up another portion of the gaseous ammonia, forming sulphide and cyanide of ammonium, and these two again unite, forming sulpho-cyanide of ammonium. The free sulphide of ammonia left remains in that form, and also the hydrate of ammonia formed by the union of ammonia with the moisture of the bone.

These changes are somewhat similar to those taking place in the destructive distillation of coal. In the carbonisation of coal and bone, although practically carried on in the same way, very different ends are sought for. The gas-maker looks to the production of a rich illuminating gas as his primary object,—the coke, tar, and ammoniacal liquor are of secondary importance; on the other hand, the contents of the retort form the chief aim of the char-maker,—the illuminating gases, with the tar and ammoniacal liquor, are bye-products only.

The bones are carbonised in a series of retorts placed horizontally in a furnace, and heated from a fire underneath. They are made of iron, with one end closed, each being 12 feet long, and in shape are similar to the letter D. At the open end is fixed the frame or mouthpiece which carries the door swung on a hinge. The door has a slight projecting rim some two inches wide, which, with the surface of the frame, are ground perfectly true; on closing, the joint is made perfectly gastight by a lever arrangement. Fixed to the frame on the upper surface is the "up-take" pipe leading to the hydraulic main. Five retorts are generally bedded in each furnace, and the setting is so arranged that, by the aid of dampers and pigeon-holes, the flame may be made to sweep equally

round each retort, so that each shall receive its full complement of heat. The spent heat finally passes to an underground flue connected with the chimney. The furnaces are all internally lined with fire-brick, and have an outer 14-inch red brick wall, the whole being bound by 1-inch tie-rods.

Each furnace, with its five retorts, is called a bench. The

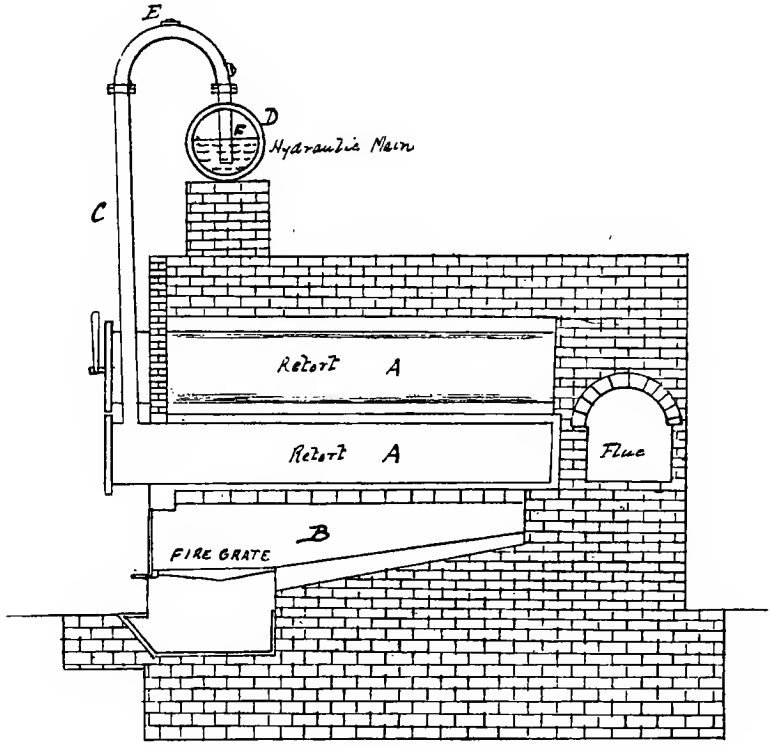



FIG. 5.

hydraulic main running along the top of the furnaces plays an important part. Not only acting as a receiver for all the volatile products of distillation, it performs the duty of a stop-valve to each retort, effectually closing it against any back-rush of gases during drawing and charging. This is

carried out by the dip-pipe connected with each "up-take" from the retorts dipping below a layer of ammoniacal liquor kept at a certain level in the main. The gases are forced through by a back pressure, and the liquor acts as a barrier in preventing their return.

Fig. 5 is a cross section of a retort bench.

*A*, *A*, are the retorts.
*B*, fire grate.
*E*, bridge pipe.
*C*, up-take pipe,
*D*, hydraulic main.
*F*, dipping pipe.

In working five benches the work is apportioned amongst four men, with the aid of a woman, to trim the bones when brought to the charging floor; each bench takes twelve hours to burn a charge, which is withdrawn in rotation. When ready for withdrawal, the door of the retort is slightly loosened by turning the lever, the escaping gases are burnt, and in a few minutes the internal pressure is destroyed, allowing the door to be opened with safety. The red-hot char is rapidly withdrawn to the "canister" placed ready to receive it, covered, and the "canister" is then rolled to the cooling shed of the mill. Here the lid is luted down with a paste of char dust and water, making an airtight joint, and the char is then cooled for twenty-four to thirty hours. Meanwhile the other retorts are being emptied by rotation, until the bench is completed. Whilst still red-hot, any unnecessary exposure coats the char with a white ash, which lowers its subsequent value after milling. Each retort is closed on drawing the charge, only being reopened to receive a fresh charge; by this means little or no loss of heat occurs between withdrawing and charging. The work is continuous, with double shifts, until a stoppage is necessary for repairs.

A bone, when well burnt, is of a deep black colour, and has a metallic ring when struck. On incineration, in contact with air, a white ash is left, which is sometimes tinged a

yellowish brown, from the oxide of iron present. The space occupied by a ton of good quality charcoal is about 50 cubic feet.

The chars found in commerce show great variation in quality, due mainly to careless manufacture. The following two analyses show this difference :—

| | No. 1. Good Char. | No. 2. Bad Char. |
|---|---|---|
| Nitrogenised carbon . . . | 10·76 | 6·83 |
| Phosphate of lime . . . | 73·50 | 70·39 |
| Phosphate of magnesia . . | 6·08 | 8·47 |
| Calcium carbonate . . . | 8·69 | 10·92 |
| Calcium sulphate . . . | ·05 | ·78 |
| Calcium sulphide . . . | ·03 | ·46 |
| Ferric oxide . . . . | ·16 | ·63 |
| Alkaline salts . . . . | ·44 | ·49 |
| Silica (sand) . . . . | ·29 | 1·03 |
| | 100·00 | 100·00 |

A good char should not contain more or less than 10 to 11 per cent. carbon, and the ferric oxide not above ·25 per cent. It is sold on a basis of 8 per cent. added water, and the dust it contains is regulated by the grade of char made.

The char, after cooling, is emptied from the canisters, watered, and is then ready for the mill, a view of which is seen in the longitudinal section of Fig. 6. The char enters the mill at *A*, an oscillating wooden trough, 6 feet long by 15 inches wide by 7 inches deep, called the "feed." The trough is fitted with five sheet-iron cross-pieces, running the full width, and equally placed, thus dividing it into six divisions. The char is thrown by portions at a time into the first division, and the oscillating movement carries it over the first iron cross-piece into the next division, and so on until the last is reached, whence it falls into the cutting-machine *B*.

The bones, however carefully sorted for the grease extractors, sometimes carry with them small pieces of iron,

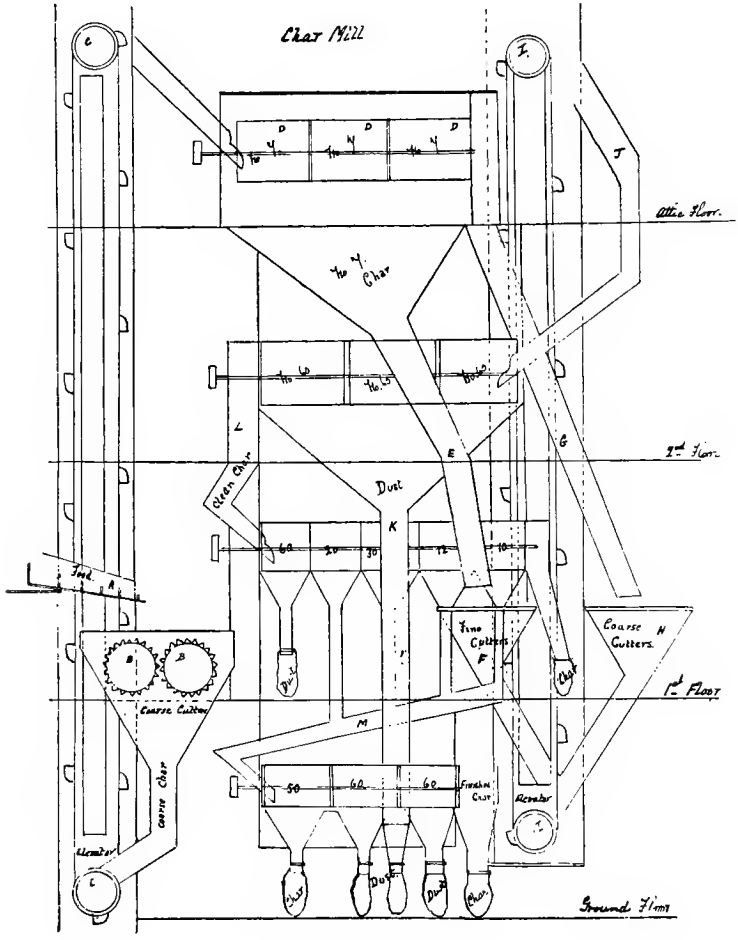



FIG. 6.

brick, etc., which, on passing to the very fine wire-cloth used in the mill, would do considerable damage. To guard against

this the oscillating arrangement is carried out, the lighter char is shaken over the iron cross-pieces, leaving behind, mainly in the first and second divisions, any heavy metal or other substance. Leaving the "feed," the char falls into a receiver, and, passing between two revolving teethed wheels, is cut into small portions about one inch long, falling thence into the "boot" of the elevator *CC*, which carries it to the revolving cylinders or riddles *D*, covered with a No. 7 cloth; this separates the fine from the coarse char, the fine passing down through the wooden "shute" *E* to the revolving cutters at *F*, the coarse char, leaving the riddles, falls down the "shute" *G* and enters the revolving cutters *H*. After a further cutting or grinding, both chars unite in the elevator "boot" *I*, and are lifted to the "shute" *J*, which passes it on to the revolving riddles *K*. These riddles are covered with a 60-mesh cloth, and are used for the purpose of sifting the char. A good proportion of dust in the char is thus separated, which, on falling to the bottom of the mill through the "shute" *L*, is bagged at *M*. The clean char then passes on to another system of revolving riddles covered with wire-cloth, to suit the grade of char to be made, and finally bagged at *N*. Passing through the cloths of a coarser mesh than 60 is also char of another grist, which is again cleansed of any dust by passage through the 60-mesh riddles *OO*, and lastly bagged for finished char. The cloths at *N* are continually changed to suit the grade required, and also extra rounds of $50^s$ or $60^s$ mesh are put on to suit the dust limit guaranteed in the grist of char being made. The taking off and replacing of the various wire-cloths is a source of loss, the cloths becoming torn and otherwise damaged. Some manufacturers remedy this by gristing four to five thousand bags of each quality likely to be in demand before changing the cloths. The following are some of the chars made, with their mechanical composition or grist:—

Grade 30/60.

| | |
|---|---|
| Size 30 | 19·13 |
| ,, 40 | 26·19 |
| ,, 50 | 33·49 |
| ,, 60 | 15·86 |
| ,, Dust | 5·33 |
| | 100·00 |

Grade 16/60.

| | |
|---|---|
| Size 16 | 5·72 |
| ,, 18 | 13·03 |
| ,, 20 | 23·84 |
| ,, 30 | 30·16 |
| ,, 40 | 14·25 |
| ,, 50 | 8·16 |
| ,, 60 | 3·09 |
| ,, Dust | 1·75 |
| | 100·00 |

Grade 10/60.

| | |
|---|---|
| Size 10 | 7·62 |
| ,, 20 | 37·50 |
| ,, 30 | 17·42 |
| ,, 40 | 16·39 |
| ,, 50 | 12·14 |
| ,, 60 | 6·82 |
| ,, Dust | 2·11 |
| | 100·00 |

Grade 12/20.

| | |
|---|---|
| Size 12 | 4·15 |
| ,, 20 | 82·89 |
| ,, 30 | 11·51 |
| ,, 40 | ·72 |
| ,, 50 | ·31 |
| ,, 60 | ·24 |
| ,, Dust | ·18 |
| | 100·00 |

Grade 20/30.

| | |
|---|---|
| Size 20 | 1·16 |
| ,, 30 | 67·11 |
| ,, 40 | 25·12 |
| ,, 50 | 3·39 |
| ,, 60 | 2·15 |
| ,, Dust | 1·07 |
| | 100·00 |

In a high-grade char the percentage passing through size 40 is limited to 2 per cent. In the grist of the 12/20 char, as seen above, this limit amounts only to 1·45 per cent., whilst in the common grade char, 30/60, it is 54·68 per cent.; 12/20 char is chiefly used in Japanese refineries. About 15 per cent. of the weight of the burnt bones from the retorts are reduced to a dust in milling. Each grade of char takes up a portion, and the remainder is bagged. Possessing little value as a decoloriser, the manufacturer converts it into superphosphates, or he can realise a better price in the production of ivory black. For either export or home use the char is packed in 2-cwt. bags.

In the hands of the sugar refiner the life of a char may be placed at two years. During this time it is continually reburnt to destroy the organic and albuminous matter absorbed

during the passage through it of light or dark-coloured sugar syrups. The destruction of this matter increases the fixed carbon, the char increases in density, becomes less porous, and ultimately its decolorising power becomes reduced to a minimum. The char then becomes what is technically termed "spent," and is generally bought by the char-maker for conversion in the manure house into superphosphates.

A sample of "spent" char gave on analysis—

| | |
|---|---|
| Carbon . . . . . | 21·62 per cent. |
| Tribasic phosphate of lime . . | 73·65 „ |

The tar and ammoniacal vapours leaving the hydraulic main are passed through a series of pipes vertically placed, and termed "the condenser." The size, height, and number of these pipes depends on the quantity of gas that has to be cooled in a given time. Generally 70 square feet of pipe surface is allowed for the cooling of 1000 cubic feet of gas per hour. The gases ascend and descend the pipes alternately until their temperature is reduced to about 80° or 85° F.; this reduction condenses the minute particles of tar with the ammoniacal gases. At the bottom, formed of the brickwork on which the pipes rest, are a number of wells, each serving two pipes, into which the condensed tar and liquor falls. These again are drained into a main pipe carrying the whole of the condensed products to the main separating tank. From the difference in gravity, the tar rises to the surface and is floated away through a discharge pipe to the tar well, and the ammoniacal liquor is pumped to the still or boiler for subsequent distillation. So that the gases can traverse the condensers with a steady and regular flow, and to relieve any great pressure in the retorts and hydraulic main, thus freeing the former from any heavy deposit of carbon, an apparatus called "the exhauster" is connected with the outlet condenser

pipe. In some works a scrubber or washer is used to wash the gases forced from the exhauster, the object being to recover any uncondensed tar and ammonia. The scrubber is built of circular steel plates bolted together, and is about 20 feet in height, with a width of 6 feet, and is supported by a structure of brickwork. Inside are a series of perforated trays, placed 14 inches apart, and carrying a layer of coke, broken into small pieces; at the top a rose pipe is fixed, which throws a spray of water equally over the surface of the first layer of coke, and thence, trickling down from layer to layer, meets with the ascending gases, dissolves out the tar and ammonia, leaving the uncondensable portion to pass out at the exit pipe placed at the top. The recovered products leave the scrubber by the exit at the bottom, and are conveyed to the main separating tank.

The uncondensable gases still require a further purification to remove the carbonic acid and any volatile sulphur compounds. For this purpose they are passed through perforated trays holding a layer of slaked lime some three inches deep, the trays being enclosed in boxes with a movable top, and built of $\frac{3}{8}$-inch steel plates. They are generally constructed 10 feet square, with a depth of 4 feet. The gases pass in at the bottom and ascend through the various layers of lime, which absorb the impurities, finally passing out at the top direct to the gasometer.

The volume of gas yielded is considerable, and in its use for lighting the works, or for motive or heating power, it plays a very important part in the successful working of a concern. The bones passing into the retort have about 6 per cent. of nitrogen. A portion of this goes to form the complex bodies of the tar; another portion is found in the illuminating gases; a further quantity is lost in actual working; and the remainder goes to build up the various ammonia compounds forming the ammoniacal liquor.

In the manufacture of cyanide of potash nitrogen forms the principal factor, and any cheap source for providing it and making it available for this purpose would be welcomed. Many attempts have been made to capture the nitrogen of the atmosphere, but with indifferent results. Better success has attended the use of high strength ammonia as worked by Beilby's process. There is, however, ample room for further improvement. Cyanide of potash presently brings about £112 per ton on a 98 per cent. basis, and the demand is increasing as the old chlorination method of extraction dies out and as new goldfields are discovered. If the char manufacturer had some means of converting the store of nitrogen in the ammoniacal liquor into cyanide, or by any method intercept the gases coming from the retorts, take away the nitrogen and convert it into cyanide instead of sulphate of ammonia, the gain to him would be considerable. Supposing, for instance, he could use only 3 per cent. of the nitrogen for this purpose, he would obtain on the 100 tons of bones calcined 11·6, say 11½ tons of cyanide of potash, and at £112 per ton would have a value of £1302. If this amount of nitrogen were converted into sulphate of ammonia the tonnage obtained would be 23·57, say 23½ tons, at £11 per ton, and only realise £258, 10s.

Undoubtedly, as chemical research in this direction progresses, means will be furnished to use the whole, or nearly so, of the nitrogen for the more valuable cyanide-making. As it is, the char-maker is now confined to the manufacture of sulphate of ammonia, realising at the best but only a moderate price, and working with only a part of the nitrogen which the bone originally had. The still receiving the ammoniacal liquor has a capacity of 6000 to 7000 gallons. It is built of boiler plate, is dished at both ends, and has a dome or still-head, to which is bolted on the 6-inch conveying pipe. Along the bottom steam pipes are arranged for boiling

purposes. Midway between the still and the "sulphate box" is a cylinder, vertically fixed on wooden supports. To the bottom is bolted on the conveyer pipe leading from the still, and the outlet pipe is fixed with a flange to the top, and then continues to the "sulphate box." The object of this cylinder is to retain any liquor "frothed" over during the boiling, and also to condense a good portion of the watery vapours; both pass back down the inclined conveyer pipe to the still. The "sulphate box" is a lead-lined, circular iron vessel covered with a hood to carry off any obnoxious gases, and fitted with a sliding door, through which the workman watches the operation, and also "fishes" out the finished sulphate. Near at hand, but at a higher level, is placed the acid storage vat, containing brown oil of vitriol, which is run by a lead pipe to the "sulphate box," the stream being controlled by a "cock" placed within easy reach of the workman. The "sulphate box" is half filled with strong acid, covering the lead dipping pipe; the gases coming from the cylinder bubble through the acid, instantly unites with the ammonia, the union being accompanied with considerable ebullition. When the saturation point is reached, the sulphate separates out in fine particles or crystals, falling to the bottom of the box, and at intervals is "fished" out by a ladle and thrown on an inclined table to drain. Now and again the workman takes a smell of the issuing vapours, and if the pungent smell of ammonia be detected, more acid is added to neutralise it.

A still requires some fourteen hours to work off the ammonia, and the residual liquor will only have a strength of about $\frac{1}{4}^{\circ}$ Twaddell.

The sulphate of ammonia produced is grey in colour, and contains on an average 95 per cent. pure sulphate. The yield is about eight per cent. on the tonnage of bones carbonised.

The value of the tar rests solely on the amount of residual pitch recovered by distillation, the yield averaging

14 lb. for every ton of bones "retorted." It is used mainly for the manufacture of black varnishes, Brunswick black, etc. The volatile products, after condensation, yield an oily liquid, to which the term "bone oil" is given. Up to the present no practical use has been found for it, excepting that it can be sprayed into the fire-grates of the steam boilers, and thus lessen the consumption of fuel.

### Marrow Bones.

Part of the raw material delivered at the works are the thigh and leg bones, termed "marrows" or "knuckles." They realise a much higher price, and are worked separately from the common bones. The first operation is the "sawing off" of the ends, leaving bare the core; the ends being passed on to the extraction house for benzene treatment. The sawn bones are conveyed to a large vat, covered with water, in which a little salt is dissolved, and allowed to steep for three days. The salt assists in the removal of any blood contained in the bone. After steeping, they are removed to the boiling vat, again covered with water, which is, by the aid of a steam coil, brought to a simmer, not higher, for six hours. Excess in boiling renders the bone "chalky" and "soft," and its value is thus considerably lowered to the button-maker. During the simmering the fat rises to the surface of the water and is skimmed into a cooler. When the steam is turned off, the water is gradually cooled to 130° F., and the bones removed; each individual bone is "scrubbed," to detach any soft "mealy" matter or dirt, by a number of girls. They are now wheeled to an open shed, spread, to the thickness of one bone only, on a rack, and allowed to dry in a good current of air, and then stacked for use. The average yield of marrow fat is about nine per cent., and a sample gave on analysis the following results :—

| | | |
|---|---|---|
| Impurities—Water . . . . . | 1·46 | per cent. |
| Organic matter (other than fat) | 0·02 | ,, |
| Mineral matter (ash) . . | 0·43 | ,, |

The clean fat had—

| | | |
|---|---|---|
| Neutral fat . . . . | 47·07 | per cent. |
| Glycerine (1·24 sp. gr.) . | 5·28 | ,, |
| Free fatty acids . . . | 52·93 | ,, |
| Non-saponifiable matter . | None. | |

Marrow fat is of a much lighter colour than benzene bone fat, and consequently brings a better price. It is used for soap-making, and also for expressing the fat oil used as an adulterant in neat's-foot and other high-class oils, and for other purposes. The following is a pressing of good marrow fat:—

Temperature of pressing, 55° F.

Marrow fat weighed 10 cwt. 3 qrs. 6 lb. and yielded—

| | |
|---|---|
| Stearine . . . . | 6 cwt. 0 qrs. 16 lb. |
| Fat oil, 57⅔ gallons, weighing | 4 cwt. 2 qrs. 15 lb. |
| | 10 cwt. 3 qrs. 3 lb. |

The atmosphere and oil, 55° F.

Pressure exerted = 150 tons.

When the bone is not an after-product for button-making, a much greater yield of fat is got by the following method:—Take the marrows, saw off the ends, and wash well with water until the visible blood is washed away, and thence place in a digester, half fill with water, previously adding 5 to 7 lb. salt for every 5 cwt. bones; and digest for eight hours, with a steam pressure of 40 lb. When digested, allow the liquid contents to run off into a receiver; the fine fat will float on the liquor containing the glue and other bodies exhausted, and on skimming is brought into the market under the name of "Premier Juice."

A few firms carry on in this country the manufacture of

buttons, etc., but the industry is mainly centred in France and Germany; and to these countries are shipped large quantities of prepared marrow bones. Not only are they makers of buttons, spoons, paper-knives, and many fancy articles from bone, but they convert the residual cuttings, rings, etc., into high-class gelatine, whilst the fine meal from the drills forms an additional source of profit, as an admixture to the food of poultry, dogs, etc.

## CHAPTER II.

### Glue.

The art of glue-making is one of the most important processes of the bone works. Glue is an impure gelatine, and has a similar composition to the cartilage from which it is obtained by boiling. The colour of glue varies according to the manufacturer's requirements. Good quality glue is practically free of any smell, is unaffected by the atmosphere, and has great cohesive power. When immersed in cold water for twenty-four hours it remains quite insoluble, while the original weight has increased four to six times by the absorption of water. With hot water glue dissolves completely, giving a clear liquor which jellies in a few hours to a firm mass. On incineration a white ash is left, chiefly phosphate of lime. Glue is perfectly insoluble in ether and all fatty oils. With concentrated sulphuric acid a rapid change takes place, and glycocine, otherwise termed sugar of gelatine, is formed; whilst heating with nitric acid produces oxalic acid. According to the nature of their origin, glues may be classified as bone or hide glues. Chemically the difference between the two rests on the amount of glutin each contains; physically, the adhesive power and elasticity of hide are greater than those of bone glue.

Of the two organic bodies, glutin and chondrin, that go to build up the constitution of glue, glutin has a much greater coherent power than chondrin, and it is in all hide glues that it predominates, being derived from hide and osseous parts, consequently they are the stronger. The chondrin, as derived

from the cartilage of the ribs, shoulder-blades, etc., is predominant in bone glue.

In a works mainly dealing with bones the production of skin glue is but a subsidiary branch; and the liquors are principally used to strengthen and give body to certain classes of bone glue made. The skins are firstly "limed" in a thin lime-water for several days, the time occupied varying according to the appearance of the skins; if soft and bluish, the "liming" is continued. On the other hand, too much steeping diminishes the yield of glue, which, however, is of excellent quality. The skins should be "firm" and free from any greasy feel before they are taken out of the lime vat. The "liming" effects the dissolving of the blood and flesh of the skins, and also saponifies the fatty matter. They are now thoroughly washed in a perforated iron cylinder, horizontally placed and revolving on its own axis. The cylinder has a diameter of 6 feet, a length of 4 feet, is open at both ends, and around the inside is fixed a number of wooden shelves 6 inches broad, which, as the cylinder revolves, carry the skins partly round, ultimately falling to the bottom again, the movement dashing them about under a heavy spray of water. In the cylinder is also arranged an iron plate, supported by stays from the outside. While the washing is in operation the plate is turned perpendicular; on completion it is brought to a horizontal position, forming a table on which the skins fall, and are then removed to a hand press to squeeze out the water.

The effluent water from the washer is heavily charged with lime, the alkalinity at times being as much as 192 grains per gallon. The water also holds a good quantity of organic matter along with the stearate of lime formed during the "liming" process, and which, if run direct into a stream, would form a source of pollution. To remedy this a large settling pond, built of brick and lined inside with cement, is

provided, the size varying according to the quantity of effluent produced daily, into which the day's effluent is run, and on the stoppage of the washer a mixture, formed by dissolving two parts ferrous sulphate and one part alum in a little hot water, is added. After stirring, the whole is allowed to settle for eight to ten hours, when the water becomes quite clear, and with safety can be run into a stream. The thick sludge is removed by pumping, dried by any waste heat in the works, and then used in the manure shed. The cost of treatment is about 11d. per 7000 gallons effluent.

The skins from the press are now taken to the glue-boiler, which is an open vessel, 8 feet diameter at the top, and 7 feet deep, and provided with a perforated false bottom, through the centre of which passes a 2-inch pipe, one end dipping below a layer of water at the bottom, the other projecting about half the height of the boiler, this part being covered with a perforated hood to spray the liquor through the mass. The skins are placed on the false bottom, and the added water at the bottom of the boiler brought to the boil by means of a steam pipe. The steam, not being able to escape quickly through the dense mass of skins above, exerts a pressure on the water, forces it through the pipe, to be sprayed through the mass, and ultimately works its way to the bottom of the boiler, to be forced up again. This continual circulation of the hot liquor rapidly dissolves the gelatinous matter, and when a strength of 18 per cent. dry glue is reached, the first run is made to the evaporating pan, the liquor passing through a filter of fine shavings, to remove any suspended matter. Fresh water is added to the boiler, and the boiling renewed. Three extractions are usually made, the last being used for size. The evaporating pan used is 6 feet square and 3 feet deep, arranged with a coil of piping, and the liquors are evaporated down to a strength of 32 to 34 per cent. dry glue, and are used as an admixture to

certain bone glue liquors, or may be jellied in coolers, cut and dried in the usual way. Some boilers add a little alum to the liquors before concentration, to precipitate any lime and remove any turbidity; the liquors thus treated must be filtered anew before evaporation; on the other hand, many boilers do not find it necessary.

In works where the bones are subjected to the benzene process, they usually undergo no other treatment after being cleansed, but are sent direct to the glue-extractors. Sometimes, however, an exception is made to this procedure, and the boiler will immerse a charge in a bath of muriatic acid, about 1° Twaddell strength, for twenty-four hours, and after washing, fill his extractor. He assumes that such treatment improves the quality of the glue; however, any slight gain here is counterbalanced by the labour and time expended, the loss of phosphate of lime dissolved, and the value of the acid used.

The system of glue-boiling varies with firms; some adopt the water system, and others the direct steam process. In the former the extractors are small, holding about 3 tons each, and generally are worked in couples, water and steam being made to play alternately through each extractor. Each couple require a plentiful supply of hot water, necessitating a special boiler for feed purposes. The liquors yielded are large in bulk, and vary considerably as regards their strength, the average being about 10 per cent. dry glue. The degelatinised bones withdrawn from the extractors are very wet, and give an inferior bone meal when dried and ground.

The following four samples of degelatinised bones, drawn at different periods, give the percentage of nitrogen, unrecovered as glue, by this process:—

| | (1) | (2) | (3) | (4) |
|---|---|---|---|---|
| Nitrogen in degelatinised bones . | 1·29 % | 1·18 % | 1·36 % | 1·24 % |
| Equal in glue to . | 7 % | 6·40 % | 7·38 % | 6·73 % |

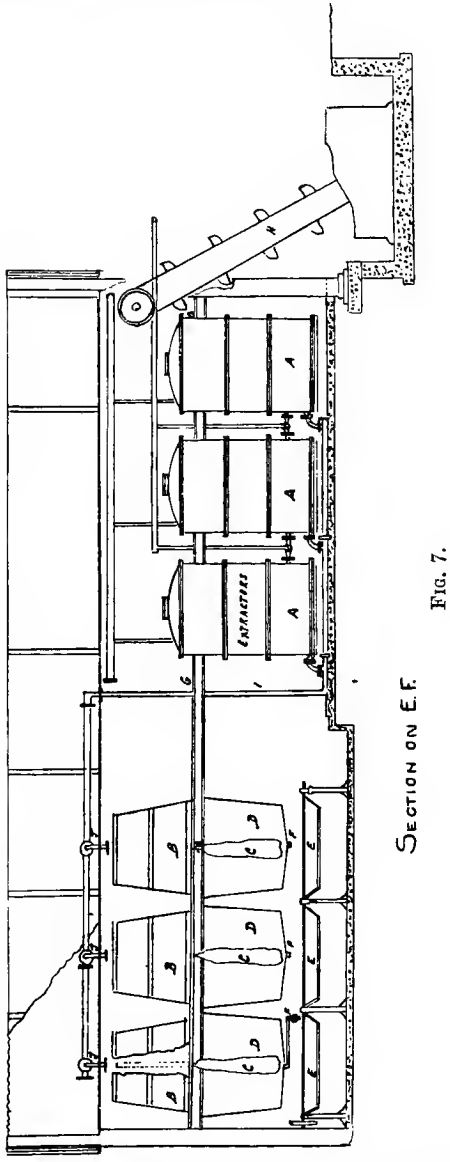
The direct steam method may be considered a more economical way of extraction. Less room is required for the plant, and it is easier worked. The liquors are less bulky, and have a higher strength, averaging 20 per cent. dry glue,—a very important advantage in the after evaporation. The bones are drier, and the bone meal is of better quality.

Of four samples of degelatinised bones, by the steam method, drawn at different times, the percentage of nitrogen was as follows:—

| | (1) | (2) | (3) | (4) |
|---|---|---|---|---|
| Nitrogen in degelatinised bones . | ·93 % | ·87 % | 1·13 % | 1·05 % |
| Equal in glue to . | 5·04 % | 4·72 % | 6·13 % | 5·70 % |

The percentage of nitrogen, which is practically unrecoverable in the form of glue, is 1 per cent. In Fig. 7 is seen a section of a glue-boiling and clarifying house, with plan of clarifying vats, filters, and evaporating troughs. The whole of the operations are carried out within one building, which is provided with an upper floor, supporting the vats, as seen in the first floor plan (Fig. 8.) This floor also carries a small railway, running the length of the extractors *A*, so that the cleansed bones, as brought up by the elevator *H*, may be rapidly discharged into them. In the plan is seen an installation of six extractors, built of mild steel plates well riveted together, and holding 4 tons each. According to the amount of size made, one or two are used for that purpose solely, the rest exclusively used for glue. On the ground floor is placed a small railway for the rapid removal of the treated bones. The liquor from each extractor is discharged into one main pipe which feeds, by branches, the different vats *B*. These are built of wood, 1¾ inch thick, and stoutly bound with iron hoops. Each vat is fitted with copper steam coils, 2 inches diameter, and is also provided

with an upright perforated copper pipe, $2\frac{1}{2}$ inches diameter,




SECTION ON E.F. FIG. 7.

passing through the bottom of the vat, and to which is fixed

a cock to shut off or regulate the flow of the liquor after the bleaching and clarifying is finished. Underneath is placed the bag filter *C*, made of medium woven calico, and having a length of $7\frac{1}{2}$ feet, the filter being enclosed in the box *D* to prevent any loss of liquor spurting out. On the ground floor are placed the three evaporating troughs, each evaporating the

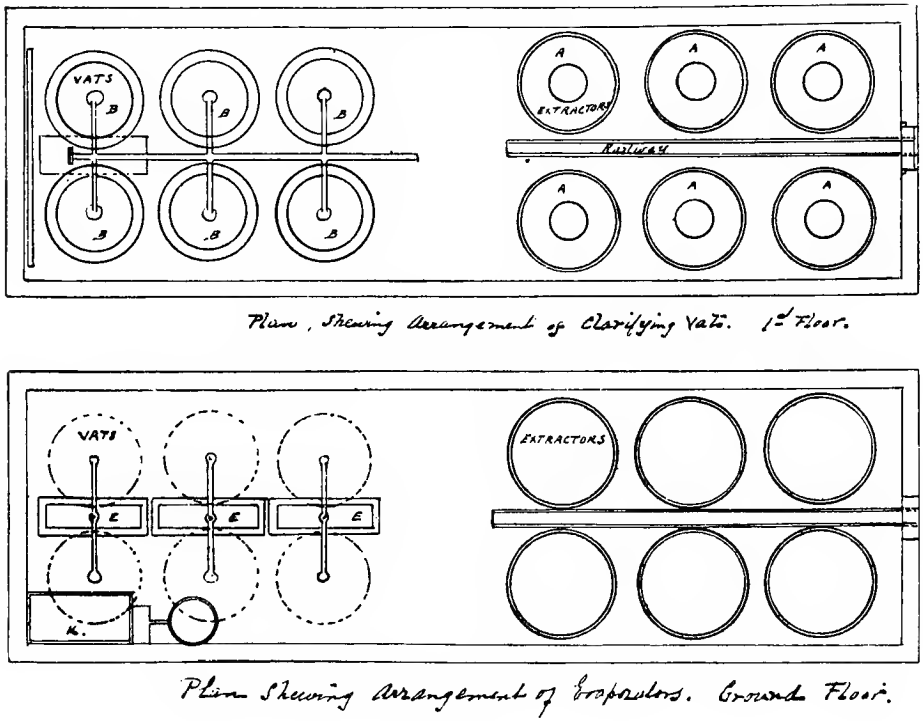



FIG. 8.

liquor from two vats. The liquors leaving the clarifying vats have a strength of about 20 per cent. dry glue, and they are evaporated down to a strength of 32 per cent. in winter, and 35 per cent. in summer. For this purpose spiral evaporators are used, forming a ready and economical means of evaporation. The evaporator consists of a spiral

steam coil, made of copper, and 2 inches diameter, revolving on a centre shaft; the lower half of the coil is covered with the glue liquor in the trough. The shaft rests on two plummer-blocks, one receiving the steam, and the other discharging the spent steam and condensed water. The shaft is hollow to the first coil, and the steam is thus conveyed to the spiral. From the last coil to the end of the plummer-block the shaft is also hollow, and in that portion resting on the block two openings are made. In the inside of the plummer-block, two openings are bored to the outside, each forming a covered channel; as the shaft revolves, all the holes directly face each other at intervals, and thus allow any condensed water in the coils to be blown through. From twenty-five to twenty-eight coils are generally used in each spiral. The glue liquors are fed into the trough at one end, and have a temperature of 75° C., the temperature of the evaporated liquor is 85° C. In the rather slow passage through the trough, the liquors receiving the heat of the revolving coils are raised in strength from 20 per cent. to 32 per cent. dry glue, at which point they are ready for jellying.

On this floor is also placed the sulphurous acid generator, a longitudinal section of which is seen in Fig. 9, and comprises an air-compressing engine *A*, throwing a current of air into the iron cylinder *B*, in which is placed a tray containing ignited sulphur. The sulphur burns to sulphurous acid gas by the aid of the oxygen of the air blown in, and is then pressed into the lead-lined wooden vessel *C*, which acts as a washer. On bubbling through the water, it is conveyed by the pipe *F* to the clarifying vats. This method of bleaching is more economical than the use of sulphurous acid, and can be so regulated that any shade of colour can be obtained at will.

In each extractor, although not shown in the section, a

"vomit" pipe, 3 inches in diameter, is placed in the centre, and supported on the bottom by three stools. The pipe runs through the false bottom to within a foot of the top of the extractor, and is fitted with a hood for spraying equally over the surface of the bones the ejected liquor. At the bottom a 1-inch steam injector pipe is led just inside the "vomit," and the end is closed with a column of water 9 inches high.

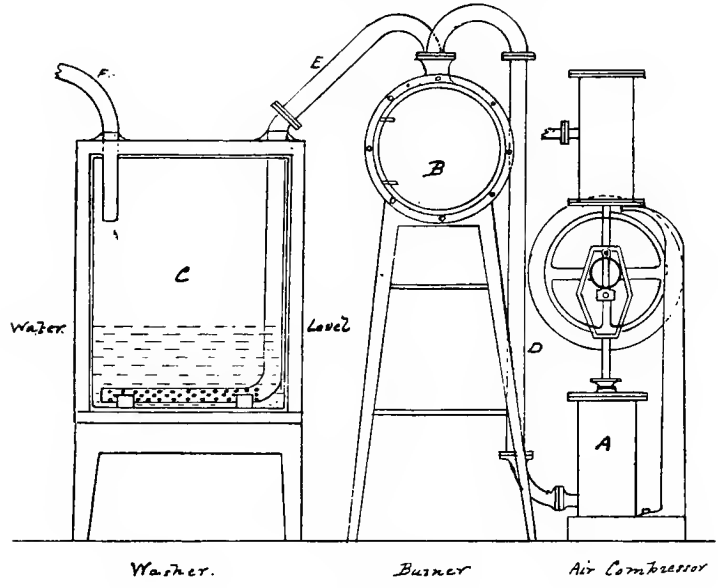



FIG. 9.

The successful working of the "vomit" pipe depends on the unequal pressure above and below the false bottom, and is used for the purpose of washing down the exuded glue from the bone. In working a charge of bones, the steam-pressure should not be raised above one atmosphere (15 lb.), and lowered from time to time down to 5 lb. This lowering of the pressure enables the formed glue within the bone to come to the surface, and washed down by the spray. To each

extractor is fitted a pet cock, which enables a sample to be withdrawn at any time for inspection. A charge usually takes about eighteen hours, and the liquors are drawn off at intervals of six hours.

On discharging from the extractors, the liquors are led to the clarifiers, treated with the requisite quantity of alum, previously dissolved in a little of the glue liquor, and kept by the steam coil at a simmer for half an hour; the temperature is then lowered to about 80° C., and the sulphurous acid gas allowed to bubble through until the desired shade is obtained, small samples being drawn from time to time for inspection. On completion, the under-valve is opened, and the liquor allowed to run into the bag filters for filtration, and from thence to the evaporating troughs.

In the clarification of glues many attempts have been made to supplant alum as a clarifying agent by the use of phosphate of soda, oxalic acid, blood, sub-acetate of lead, infusion of bark, etc., but little success has attended the efforts. Alum, when used in excess, is undoubtedly injurious to glue; but in the small proportions necessary for clarification, its use cannot be considered as harmful to the glue.

The concentrated glue liquor leaving the evaporators is jellied by running into sheet-iron troughs, called coolers, and allowed to stand in a cool place for twenty-four hours; or, if the glue made is what is called a cast-glue, it is run on to glass coolers, at a required thickness, and jellied, thence cut into cakes and dried. Cut glue has a better appearance than a cast-glue, although it may not be a stronger glue.

One of the most difficult operations of the glue-maker is the drying of the glue. The temperature of the air and its humidity have to be carefully watched and guarded against. Glue will not bear a higher temperature than 20° C. (78° F.) when in the jellied state, otherwise it will run through the nets. On the other hand, an excessive humidity in the

atmosphere prevents the jelly from drying, and in a short time it becomes mouldy.

In Fig. 10 is seen a longitudinal section, with upper and ground floor plans, of a modern drying-house. In the ground floor the whole of the liquors are jellied in coolers, and thence cut into cakes by the two cutting machines in the centre. Here a hoist *E* (p. 44) is placed, which carries the cut cakes on "glasses" to the floor above. This forms the drying-floor, and is partitioned off into three divisions, running nearly the length of the building. The two outer divisions form the tunnels proper, and at the ends are fixed two powerful revolving fans, driven at high speed, and drawing the air through the tunnels at a high rate. At the opposite ends to the fans are fixed a series of 6-inch pipes, heated up by waste steam; and the air passing between is warmed up to any desired temperature, of necessity below 78° F. In the centre passage a number of girls are employed in transferring the cut cakes to the nets, which are built up on a carriage running on a small railway. The carriage, with its complement of filled nets, is run to the end of the division, transferred to the lower railway *C*, by which it is carried either to the right or left hand tunnels as desired; the glue, when dried on the nets, is run to the other end, and by another lower railway brought to the middle division, and ultimately by the hoist raised to a large storeroom, seen in section, where the glue is sorted and bagged. At the end of the store is placed a grinding machine, and all the off-colour and twisted cakes are ground to a powder and sold as powdered glues. The manufacturer, by varying the size of the cake, its thickness, and its colour, may make any number of grades from the same boiling of bones.

The appearance of a glue is no indication of its strength. A glue may be quite clear and bright, and show good shrinkage, yet it may have but medium adhesive power. On the other

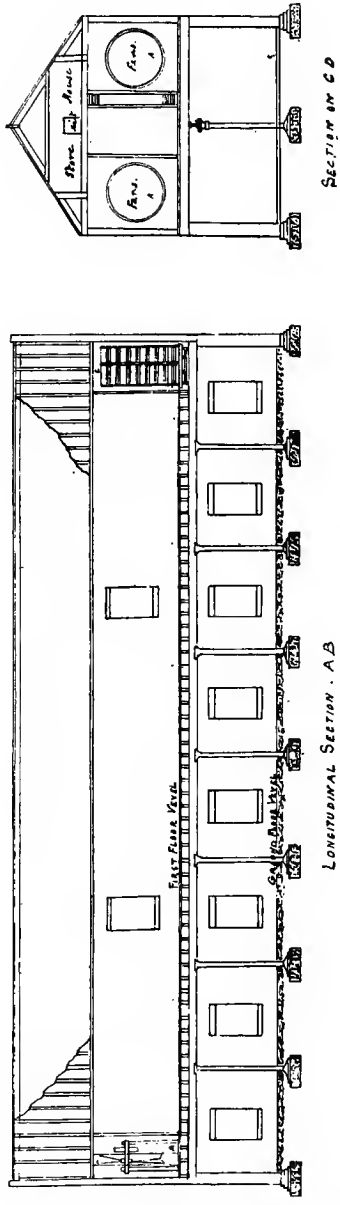
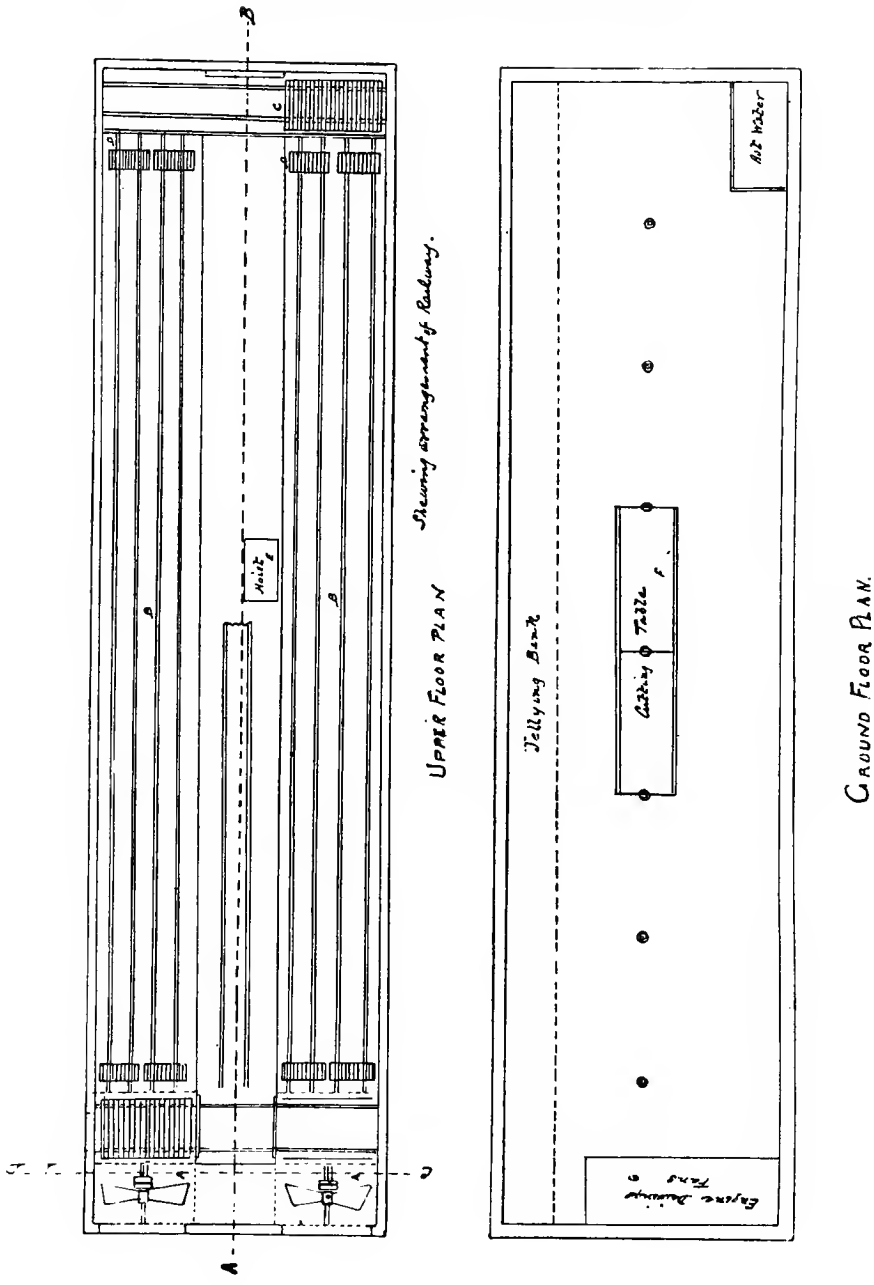



Fig. 10. (See also p. 44.)

[See next page for Upper and Ground Floor Plans.


Showing arrangement of Railway.
Upper Floor Plan
Ground Floor Plan.
Hoist
Hot Water
Cutting Table
Engine Driving Pulley

hand, a dull, heavy-looking glue may have greater strength and be more valuable to the user. A good glue should break sharp, with a glassy fracture, should be brittle and hard, and quite transparent. A good practical test for the consumer is to take a portion and dissolve it in eight times its weight of hot water, and allow it to stand for twelve hours. The resulting jelly, if made from a good glue, will be firm and withstand the pressure of the fingers.

The following should comprise the specification of a good bone glue :—

(1) The sample shall take up at least four times its weight of water, when a known weight is placed in cold water for twenty-four hours.

(2) That the jelly so formed shall be firm and consistent and cohesive.

(3) That the viscosity of a 1 per cent. solution at 18° C. shall be twenty-nine seconds when run through a burette, taking water at twenty-five seconds.

(4) That an 11 per cent. jelly, made by dissolving the glue in hot water, and then allowing it to stand for twelve hours, shall bear a weight of 15 grams (plus the funnel, which weighs 10 grams) at a temperature of 18° C. (shot jelly test).

(5) That the sample shall possess no unpleasant smell when dissolved, and the solution shall develop no fungus when allowed to stand six days in the cold.

(6) That the sample shall not contain more than ·20 per cent. sulphurous acid, or sulphites, or mineral acid.

### Size.

The demand for some agglutinous material which, while it possesses the adhesive properties of a glue, shall be easier of assimilation with water, and obtainable at a much

more reduced price, has brought into existence a commercial article to which the name "size" has been given. Size is simply an undried glue, and, in the commoner qualities, a very impure product. The same chemical properties in glue made from bone or skin naturally exist also in size made from the same source. In glue, they are concentrated; in size, the reverse The proportion of water in one will range from 10 to 13 per cent.; in the other, a common quality will carry 75 per cent., and thus enable a manufacturer to sell at from £5 to £6 a ton. Many firms who have a good selling connection for size, do not go to the expense of erecting clarifying plant and drying-house for treating the glue liquors, but prefer to stop the process of glue-making half-way, as it were, and marketing the resulting product as size. Others again, with a complete glue plant at hand, convert only a portion of their liquors into size, to meet trade demands, the bulk going for the manufacture of glue. Size varies in quality to suit the requirements of different trades. Cardboard box-makers prefer a strong skin size, which is manufactured red or yellow, as preferred. A strong yellow size made from bone is used by calico printers, paper stainers, wall-paper manufacturers, and in the straw hat and carpet trades. Common size finds various markets as a cheap agglutinant. In the preparation of skin glue the first and second liquors are used for that purpose; the residual mass is then treated with water and steam, which practically exhausts the gelatinous matter. This, the third liquor, is used solely for size. During the boiling, samples are taken at intervals, cooled, and the condition of the jelly noted. The strength is also taken by the glue meter, which registers the percentage. At a strength of 8 to 10 per cent. the liquor is run off, passing through a filter of fine shavings or cloth, to remove any suspended matter into a wooden vat fitted with a steam coil, then treated with

a moderate charge of sulphurous acid to bring up the colour, and evaporated to a strength of 36 to 38 per cent., as may be desired, and then run into casks to jelly.

If skin glue is not made, the three runnings are used entirely for size.

In preparing bone size, the bones are first degreased by the naphtha process, and then passed through the cleanser direct into the glue boilers, and steamed as in the manufacture of glue; the resulting liquors, forced up to the clarifying vats, and partially bleached with a current of sulphurous acid, passing thence through the bag filters to the evaporating troughs, and concentrated from 30 to 38 per cent. as required, and then jellied in casks.

The manufacturer with no benzene or glue plant at his disposal, washes the bones in a revolving drum, and, after crushing, they are fed into a boiler and subjected to an alternate current of steam and water, the latter coming from a spray pipe fixed at the top of the boiler.

The liquors are generally drawn in two portions, having a strength of 14 to 16 per cent. of glue. After separating the fat, which is refined and sold to the soap-maker, the liquors are run into a large wooden vat ($8' \times 6' \times 4'$) fitted with a steam coil, partly bleached with liquid sulphurous acid, and then boiled down to the required strength.

For a common size the bones are crushed, but unwashed, and are fed direct into the boiler and treated as above. The liquors are unbleached and boiled to a strength of about 25 per cent. glue.

The composition of the different grades may be given as follows:—

| | | |
|---|---|---|
| Common size | 25 per cent. | glue. |
| | 75 „ | water, etc. |
| Medium size | 30 „ | glue. |
| | 70 „ | water. |
| Best size | 38 „ | glue. |
| | 62 „ | water. |

A concentrated size is now prepared by many manufacturers. It is a bone size, and finds a ready market in France and Spain, and is sold on a Baumé strength at 50° C.

| | |
|---|---|
| No. 1 . . . . | 15° Baumé at 50° C.<br>40·5 per cent. glue. |
| No. 2 . . . . | 20° Baumé at 50° C.<br>44·5 per cent. glue. |
| No. 3 . . . . | 25° Baumé at 50° C.<br>49 per cent. glue. |

Under the name of concentrated size also are sold a series of powdered glues of different qualities. They are the off-colour and twisted cakes, sorted out in the warehouse, and ground to a fine condition by passing through a mill, and their value is based on the quality of the cake ground.

As is well known to makers, size rapidly ferments, and becomes sour and mouldy, unless some preservative is added. For this purpose sulphate of zinc is mainly used. Other preservatives, under the names of "Salinfer," "Preservatine," have also been employed with good effect.

## CHAPTER III.

### GELATINE.

GELATINE may be considered as a pure glue. It is quite transparent, has a slight yellowish tint, and is very hard and elastic. When immersed in cold water for twenty-four hours, it softens and swells, but does not dissolve, and loses its transparency, becoming opaque. Similar to glue, gelatine has the power of mechanically absorbing water on immersion, the absorption being, in good qualities, as high as 8 to 9 times the weight of the gelatine immersed. In hot water it dissolves completely, and on cooling for twelve hours an almost colourless, transparent, and very firm jelly is produced. This power of gelatinisation is, however, partially destroyed if the solution is boiled for several hours. The action of concentrated and dilute acids, excepting acetic acid, on solutions of gelatine greatly differ.

Concentrated acids entirely change its chemical constitution, whereas dilute acids have no appreciable effect either on the coagulating or the adhesive power. Concentrated acetic acid, on the other hand, does not destroy the gelatine, but merely dissolves it. One of the most delicate actions with gelatine is by tannic acid; even with only $\frac{1}{5000}$th part present, nebulosity appears. The combination is of a definite nature, consisting of, in 100 parts, 42·74 parts glutin and 57·26 parts of tannin.

Like glue, gelatine has its origin in hides and skins and bones. The gelatine resulting from the former, is made by a different treatment to that which the bones undergo; the

latter yield the larger quantity of gelatine produced for consumption, either as food or for trade purposes.

In this country the manufacture is not carried on to the same extent as in France and Germany, due in some measure to our variable climate and a preference, which is exercised with less technical skill, given to the conversion of all liquors into glue and size, as more marketable products. The raw materials are selected with the greatest care and judgment, and must be quite fresh; the skins—preferably those of calves and sheep—are cut into pieces by a machine in which a number of knives are fixed to a revolving shaft, then thoroughly cleansed from any blood by soaking in a brine solution of 3° Twaddell strength, afterwards washing well. The bones used are mainly the ribs and jaws, and are also well washed before using.

The clean waste cuttings and rings from the button factories further furnish their quota of gelatine.

### Skin Gelatine.

Since Nelson introduced his method of preparing gelatine from skins, very little change has been made in the process of manufacture. The first treatment the cleansed skins undergo is the "steeping" process with caustic soda or milk of lime. In some factories a mixture of caustic (slaked) lime and soda ash is used, in the proportion of 6 lb. soda ash and 6 lb. slaked lime to every hundredweight of skins treated; the chemical change being that the whole of the carbonate of soda (soda ash) is converted into caustic soda by its equivalent of caustic lime, the excess of the latter remaining as such. The equation representing this is—

| $Na_2Co_3$ | + | $CaH_2O_2$ | = | $2NaHo$ | + | $CaCo_3$ |
|---|---|---|---|---|---|---|
| Soda ash. | | Caustic lime. | | Caustic soda. | | Carbonate of lime. |

The steeping is conducted in large wooden vats, each having

a length of 12 feet, width 8 feet, and depth 3 feet, and fixed with a slight gradient to the overflow, which is placed at the most convenient corner of the vat and protected by perforated boards. The skins in the vats are nearly covered with water, and then the solution of caustic soda, or the slaked lime mixed in water to a cream, is sprayed equally over the mass, the whole being intimately mixed with long stirring poles. The water is renewed twice during a period of twelve days, the time allowed for the skins to soak. They are now removed to a chamber, in which a moderate increase of heat facilitates the saponification of the fat and the dissolving of the fleshy matter. The chamber is a brick building, with a cemented floor, on which the skins are spread to a uniform depth of about 6 inches, and is heated by steam pipes running round the building. At a temperature of about 70° F. the skins are exposed two or three days, with frequent turning. They are now transferred to the washing machine—similar to the one described under "Skin Glue"—and washed until the effluent is practically free of soda or lime. The skins then undergo a bleaching operation to whiten, and thus destroy any injurious colouring matter. For this purpose the washed skins are removed to a number of vats fitted with folding covers, and treated to a solution of sulphurous acid of $\frac{1}{2}$° Twaddell strength, for twenty-four hours, each vat being well stirred at intervals to allow the "bleach" to permeate equally the mass.

In some factories this process is carried out with dry sulphurous acid, the gas being generated in a sulphur burner, and, after washing, passed into a chamber containing the skins. The vats are now drained, then filled up with water, well stirred, and the water run off. This is repeated until the effluent is practically free of any sulphurous smell, and then the work of dissolving the gelatine is proceeded with. The digesting of the skins is carried on in stoutly built

circular wooden vats, each having a size, generally, of 4 feet 6 inches diameter and 6 feet deep, and fitted with $2\frac{1}{4}$-inch copper steam coil. The vats are provided with a double wooden bottom to divide the heat. They are arranged on the first floor of the building, the liquors running through a shallow filter of fine copper gauze to the clarifying vats beneath. The skins are raised by an elevator and fed direct into the vats by suitably arranged troughs, then covered with water and steam sent through the coils. The temperature is frequently taken by the thermometer, and should never exceed 177° F. (80° C.). During the digestion, any unsaponified fat and dirt comes to the surface as a scum, and is carefully skimmed off from time to time. Samples are also drawn of the liquors, cooled, and the appearance and strength of the jelly noted. After five to six hours heating, the first liquors are run off to the clarifying vats, at a strength of about 17 per cent. gelatine.

The vats are refilled with water, and a second digestion made, the liquor running to the clarifying vats at a strength of 12 per cent. In the third digestion the temperature is raised a few degrees, to practically exhaust the gelatinous matter, and can either be clarified to form an inferior gelatine or concentrated for size. The exhausted matter is taken to the manure-shed for mixing purposes. The clarifying of the first and second liquors—and if used for gelatin, the third liquor—is done separately in the clarifying vats. The clearing agent used is alum, to the extent of $\frac{1}{2}$ per cent., or a little blood diluted with water; both are mixed with a small portion of the hot liquors in a bucket, and then well stirred in the vats. The liquors are raised to 177° F. (80° C.) to coagulate the impurities, and then lowered to 149° F. (65° C.), and allowed to stand for two hours. During this time the coagulated matter rises to the surface, and is skimmed off. On leaving the vats the liquors are filtered

through fine copper gauze into a receiver, from which is fed the vacuum pan.

Gelatinous liquors being peculiarly sensitive, especially as regards colour, to high temperatures, it is found advisable to evaporate them in vacuo; and this method is adopted by all continental makers. The three grades of the liquors, concentrated to the required strength, are run on to squares of glass, $4' \times 4'$, fixed in a wood framing, to a depth of $\frac{1}{2}$-inch for cake and $\frac{1}{4}$-inch for leaf gelatine, then placed perfectly level on racks for jellying. In twenty-four hours the jelly is firm, and can be easily cut to the desired size of cake or leaf wanted. A very fine gelatine is produced by cutting the jelly into small pieces, washing well with cold water, and remelting at a temperature of 80° C., and poured again on the "glasses" for jellying.

The drying is carried on by exposing the cut cakes, on nets fixed to a framework of wood, to a rapid current of dry air in the tunnels, as described in the drying of glue.

## Bone Gelatine.

The preparation of bone gelatine depends on the dissolving out of the phosphate of lime by an acid.

The bones for the purpose are carefully picked, and those of a soft and spongy nature selected, for the greater percentage of gelatine-forming nitrogen they contain.

After well washing, to remove any extraneous dirt, in the revolving washer, as described under "Skin Glue," they are fed into a machine called a "cracker," the revolving arms or cutters breaking them into pieces about an inch long, this size facilitating the after process of dissolving. The crushed bones are then carried by a conveyer to a series of large wooden dissolving vats over which the conveyer passes, and thus the stream of bones can be dropped into any of the vats

as desired. They are filled three parts full, and then covered with a solution of hydrochloric acid of 10 per cent. strength. The acid plays a very important part in dissolving out the phosphates of lime and magnesia, the carbonate of lime and the oxide of iron forming the osseous structure of the bone, leaving the gelatinous matter intact. The "steeping" is carried on for four or five days, or until the bones become soft and leathery and semi-transparent. The acid water is now drained off, and a supply of fresh water added and then discharged. This is repeated until the last water is entirely free of acid, which is known by adding a few drops of silver nitrate; the absence of any white precipitate, soluble in ammonia, indicates its freedom.

The bones are now bleached in the manner as described under "Skin Gelatine," and then conveyed to the boiling vats. (See "Skin Gelatine.") During the action of steam and water the fatty matter floats to the surface, and is skimmed off from time to time. The gelatinous liquor is treated as described, run into glass moulds, jellied, and dried, similar to skin gelatine.

Some gelatine-makers on the Continent have given consideration to the use of bisulphide of carbon as a solvent for the fat in the bones before they are subjected to the acid treatment. The very low boiling-point of bisulphide (considerably under that of water) would not injure the gelatine in the same manner that benzene (with a considerably higher boiling-point) would. Then, again, bisulphide leaves not a trace of smell in the degreased bones.

These and other considerations have been favourably considered by French makers. There is no doubt that this solvent will play a leading part in the manufacture of gelatine in the early future.

## The Testing of Glues and Gelatines.

It may be truly said that the best test of a glue is the amount of work it will accomplish. As a cement, an inferior quality has a low binding power, and on dissolving will, in many cases, emit an offensive odour. The percentage of chondrin also will be relatively high. On the other hand, a strong glue is pure, and possesses high adhesive properties, due to the larger proportion of glutin.

All glues are combinations of two distinguishable chemical constituents, viz. glutin and chondrin. The former is derived from the skins and osseous parts; the latter is largely found in the cartilage of the ribs, joints, larynx, etc. As glutin has a greater adhesive power than chondrin, it should be the aim of the glue-maker to increase the former and decrease the latter as far as practicable.

Pure dry glutin is a yellowish transparent and elastic substance, very hard, and possessing great coherence. It is without smell, and insipid to the taste. Being neutral in its action, it exerts no influence on the most delicate colours. In cold water it is perfectly insoluble, but softens and swells as ordinary glue. With warm water, glutin dissolves completely, and from the aqueous solution may be precipitated by alcohol, tannic acid, and platinic sulphate. The solution, however, is not affected by hydrochloric or acetic acids, alum, acetate or sub-acetate of lead, or sulphate of iron. Chondrin, in the dried state, is a hard, clear, horny substance, with a specific gravity heavier than water. Like glutin, it softens to a jelly, and is insoluble in cold water; with warm water it is completely soluble.

Chondrin is precipitated from its aqueous solution by hydrochloric, sulphuric, nitric and phosphoric acids, redissolving in an excess of the acid. The organic acids—tartaric, oxalic, citric, lactic, and succinic—precipitate chondrin also

but the precipitate is not redissolved by an excess. Chondrin is distinguished from glutin by its precipitation with alum, acetate and sub-acetate of lead, and sulphate of iron, these reagents having no action on aqueous solutions of glutin. The glues of commerce are derived from hides, skins, or other glue-yielding products, or from bone cartilages. The strength of a skin glue is greater than that of a bone glue. The difference between the two kinds may be detected by breathing on the cakes. Skin glue gives no odour; from bone glue a faint characteristic smell is noticed. They should be totally insoluble in cold water, yet have the power to absorb it to several times their own weight. All good quality glues dissolve at a temperature of 62° to 63° C.

In selecting a glue, many buyers consider only the physical aspects—the shrinkage of the cake, its colour, and, in a rough and ready way, the strength of a jelly made therefrom. These tests are not always a safe guide to the value. A glue may show a good shrinkage, be perfectly clear, glossy, and hard, and yet be found very weak, owing to a low percentage of glutin.

In the laboratory of a glue works, a full testing of each boiling should be carried out, and entered, with a number and date, into a book specially kept for that purpose. The tests should embrace—

(1) Moisture.
(2) Glutin.
(3) Viscosity.
(4) Ash (and qualitative examination).
(5) Acidity.
(6) Water-absorbing power.
(7) Strength of jelly (shot jelly test).

The chemist also should examine the external aspects of the sample—the shrinkage and colour.

*Moisture.*—The percentage of water is determined by exposing a weighed quantity of the sample, finely powdered, to a temperature of 105° to 110° C. for fourteen hours, then cooling under the dessicator, and reweighing. From the loss in weight the calculation is made.

*Glutin.*—The glutin is determined by immersing a weighed portion in cold water, frequently stirring and changing the water, until all the colouring matter is extracted; then dissolve in hot water, filter and precipitate the glutin in the filtrate with a solution of tannic acid. The dense white precipitate formed is thrown on to a tared filter, washed with hot water, dried, and weighed. The calculation is made on the basis that tannate of glutin has a percentage composition of—

| | |
|---|---|
| Glutin . . . . | 42·74 |
| Tannin . . . | 57·26 |
| | 100·00 |

The percentage of glutin in a glue naturally varies according to the quality and origin. A good bone glue will yield 50 to 52 per cent.; in skin glues it varies from 65 to 75 per cent.

*Viscosity.*—The viscosity is based on the length of time required by a glue liquor of known strength to flow through a burette, as compared with water, taken at twenty-five seconds in flowing through the same. For this purpose a 1 per cent. solution of the glue is made and cooled to 18° C., thence run through the burette from 0 to 50 c.c., and the number of seconds noted. The weaker the glue liquor, the nearer it approaches the twenty-five seconds as the water standard,—that is, the quicker is the flow. On the other hand, a high quality glue dissolved to the same percentage strength forms a denser solution, and consequently runs slower through the orifice of the burette. With water as a

standard of twenty-five seconds, a poor glue will average twenty-six to twenty-seven seconds, a medium twenty-eight to thirty seconds, and a good strong glue thirty-two to thirty-four seconds.

*Ash.*—A portion of the sample is finely powdered and then weighed in a tared constant crucible, thence slowly heated over the bunsen flame until carbonised; the crucible is then removed to the muffle and heated to bright redness for ten hours, cooled under the dessicator, and weighed. The increase in weight of the crucible is the ash of the sample. This will vary from 1 to 2 per cent. in a gelatine, 2 to 3 per cent. in a good glue, to 6 to 8 per cent. in a common quality. The ash is mainly examined for phosphates of lime and magnesia; bone glue contains both; skin glue is free from phosphates. Thus the origin of the sample can be traced.

*Acidity.*—Kistling determines the acidity by suspending 30 grams of the sample in 80 c.c. of cold water for ten to twelve hours in a flask connected with a condenser. The volatile acids are then driven over by a current of steam into a graduated cylinder. When the distillate amounts to 200 c.c., the distillation is stopped, and the distillate treated with standard decinormal alkali. When the distillate contains sulphurous acid, a known quantity of the standard alkali is previously added to the cylinder.

*Water absorption.*—28·349 grams (= 1 oz.) of the sample are weighed in one piece and immersed in cold water (39° F.). If the cake is thin, twenty-four hours are sufficient; for a thick cake forty-eight hours are necessary for a full absorption.

After immersion the cake should be clean at the edges, firm, and consistent. Carefully remove from the vessel used, drain from all superfluous water, and weigh. The increase is the weight of water mechanically absorbed by the glue. The more consistent the jelly is, the greater will be the adhesive

power, and the larger the water absorption, the more economical is the glue in use. In a poor and imperfectly clarified glue this increase will be very low, the jelly soft and flabby, and the water highly turgid. The absorption will vary from one and a half to two in a common quality, to four to six times the weight in a medium glue. A strong glue will absorb six to seven, and a gelatine will range, according to colour, from eight to ten times the weight.

*Strength of jelly* (*shot jelly test*).—This test, originally proposed by Lippowitz, is based on the weight-sustaining power of a jelly of known strength and temperature. It is made by covering one end of a small glass cylinder with a tin cap perforated in the centre. Through the perforation is passed freely a stout iron wire, at the lower end of which is soldered a piece of tin dipped like a saucer, the convex side resting on the surface of the jelly. To the upper end is also soldered a similar shaped piece of tin, to hold the weight necessary to force down the wire. The whole apparatus should weigh about 10 grams. The test is made on an 11 per cent. jelly at 18° C. For this purpose 28·34 grams (1 oz.) of the sample are dissolved in 255 c.c. of hot water, and allowed to stand in the cylinder for twelve hours to form the jelly. The apparatus is gradually loaded with weights until the convex side of the saucer-shaped piece of tin is forced into the jelly. The greater the strength of the jelly the heavier will be the weight required. A medium to good quality at the above strength and temperature will carry 15 to 20 grams.

In some recent researches, Setterberg and Cronquist have suggested a novel means of testing the tenacity of a glue. They soak unsized paper with a solution of the glue that has to be tested, and then ascertain its strength or solidity by a paper-testing machine.

S. Levites, in a paper read before the St. Petersburg Polytechnic Club (1899), advocates the determining of the melting-point of a jelly as the most suitable method of obtaining the value of a glue; and later, in the *Chemiker-Zeitung*, Kistling, working on the same lines, urges the gelatine solidity and melting-point as the best criterion of the adhesive power.

However interesting these researches may be from a chemical standpoint, it is unlikely that they will be regarded as infallible by those who, from their practical knowledge, are most competent to judge the commercial value of a glue.

## CHAPTER IV.

### Uses of Glue, Gelatine, and Size.

In very many branches of industry, an agglutinant, whether glue, gelatine, or size, plays a more or less important part in the working.

Commencing with the great textile trades, the consumption of both glue and size is considerable in the dressing and finishing of coloured yarns and threads, the sizing of worsted and other woollen warps, the printing of fabrics, etc.

In the paper and bookbinding trades, the manufacture of cardboard boxes, millboards, *papier maché*, and the sizing, applying of colours, and varnishing paper-hangings, the amount is large. For fancy and ornamental work, such as imitation leather wall coverings, fire, stove, and draught screens, imitation sculpture, mosaics, paraquets, picture frames, gilding, etc., an agglutinant performs an important part.

In joinery, carpentry, and cabinet work, the putting together of railway and tramway vehicles, shop, house, office, and school fittings, household furniture, organs, pianos, billiard tables, vencering, panelling, and ornamental work in ships' saloons, the manufacture of wooden pipes, columns, and masts, etc., the glue-pot is a necessity.

For waterproofing and preserving tissues and fibres, ropes, cords, and twines, and in the preparation of transparent tablets for advertising, emery paper, substitutes for caoutchouc and gutta-percha, and in the utilisation of leather waste for making heels for boots and shoes, door and other

knobs, finger plates, door panels, plaques, trays, and even reels for sewing, glue again comes into play.

Gelatine has a more limited use in the arts. For confectionery and culinary purposes, and as a substitute for isinglass in the clarification of wines and beers, a quantity is used. Also in the dressing of white fabrics, silk, and white straw hats, and the preparation of copying pads and photographic emulsions.

### Soluble and Liquid Glues.

These are mainly combinations of glue with some ingredient, added to destroy the gelatinising property and yet not impair its adhesiveness. They remain for a long time clear and syrupy, and are used for a variety of purposes.

(1) Fifty parts of glue of a light colour are dissolved in fifty parts by weight of hot water, in which fourteen parts of fused magnesium chloride have been dissolved. The solution, on cooling, does not gelatinise, but remains syrupy, the density varying according to the quantity of water used. In the preparation of printing inks, it can be used as a substitute for gum.

(2) Ten parts of strong phosphoric acid are diluted with an equal weight of water, and then four parts of ammonium carbonate gradually added in the dry state. When the effervescence has subsided, add a further five parts of water, and warm on the water bath or steam chest to 70° C.; now add twenty to forty parts of glue, according to the consistency required, and stir until all is dissolved. Cool.

(3) Twenty parts of glue are dissolved in an equal weight of hot water, then cautiously pour in, with stirring, four parts of strong nitric acid, warm until the nitrous fumes have been driven off, filter, if necessary, through fine shavings, and allow to cool.

(4) Dissolve ten parts of glue in seven parts of moderately strong acetic acid, to which one part of alcohol has been added, and filter.

(5) In sixteen parts of hot water are dissolved eight parts of good glue, then add half to one part of hydrochloric acid, and one and a half part of sulphate of zinc. The mixture is kept at 70° C. for eight hours, then filtered through fine shavings, and allowed to cool.

(6) Eight parts of molasses, twenty-four parts of water, into which two parts of slaked lime have been mixed to form a thin cream, are heated on the water bath or steam chest for twenty-four hours; allow the lime to settle, and then decant the clear liquor, into which dissolve a half to three-quarters of its weight of glue along with 2 per cent. of its weight of glycerine. Stir well, and allow to cool.

Other preparations are in use under different names, but their composition varies but little from the above recipes. Nearly all are based on the solubility of glue in an acid and the retaining of the liquidity in a cooled state. All liquid glue should be clear and sparkling. On the other hand, the various kinds of cements in which glue forms a leading ingredient, the gelatinising property is left unimpaired, the glue being directly combined with some earthy or metallic oxide to give a body. Such cements set quite hard in a few minutes. Under this category may be placed the white (Russian), chrome, steam, and waterproof glues, and many of the cements used for binding purposes in leather, china, and glass-ware, electrical and chemical apparatus. The so-called marine glues of commerce are mixtures of benzene, petroleum, spirit, or naphtha with indiarubber, shellac, or asphaltum; they contain no glue.

Chrome and white Russian glues are prepared by adding pigments to the concentrated glue liquors before jellying. In a mixing for chrome glue 3 per cent. of chromic

oxide is used, and in a white, 6 per cent. sulphate of lead or 8 per cent. zinc oxide.

### Steam and Waterproof Glues.

The former is a liquid glue, thickened with 10 per cent. of its weight of sulphate of lead ; and a good composition for the latter is a mixture of eight parts glue, four parts linseed oil, and one part litharge.

Compositions of glue and glycerine, forming an elastic mass, are used for the making of printers' rollers, book-binders' glue, and in the manufacture of plastic masses for children's toys, etc.

# PART II.—MANURES.

## CHAPTER V.

### Soils and Plant Life.

No branch of industrial inquiry is of greater importance than that which teaches us to increase the production of the soil.

As the rich soil of a country becomes exhausted through centuries of crude agricultural working, so agriculture declines if no means are taken to restore by artificial means that wealth of nutriment which it formerly possessed, and, as it declines, so must the nation's money be increasingly spent abroad to supply the necessary food. That this is considerable may be seen from the following:—

In 1898 we imported the following food-stuffs:—

| | |
|---|---|
| Barley | 24,301,185 cwt. |
| Oats and oatmeal | 16,632,467 ,, |
| Maize and maize meal | 58,143,404 ,, |
| Beans and peas | 4,311,713 ,, |
| Rye | 1,054,969 ,, |
| Buckwheat | 173,560 ,, |
| Hay | 2,320,000 ,, |

During the same period in animal food we imported—

| | |
|---|---|
| Beef | 370,000 tons. |
| Mutton and lamb | 190,000 ,, |

We essentially are a manufacturing nation, depending on the weaving of calicoes, building of ships and machinery, the smelting of iron, and a thousand and one other industries, and we must thus look to the rising generation of farmers to reduce this enormous importation of food-stuffs, by gaining a better chemical and physical knowledge of the soil, by

studying the functions of plant life and plant food, and the judicious application of manures.

In this chapter we shall treat of soils, their nutritive and productive power, along with plant life and food.

## Soils.

Soils, from a chemical standpoint, are composed of silicious matter—fine particles of rocks disintegrated by the action of frost and water—carbonate, phosphate, and sulphate of lime, oxide of iron, potash, chloride of sodium, and silica, with decayed vegetable matter. Mechanically they may be considered as mixtures of sand, clay, calcareous marl or clay, and vegetable mould, and as one or the other predominates, we have a sandy, clayey, calcareous, or loamy soil. In 100 lb. weight of soil, these ingredients will vary as follows:—

| | |
|---|---|
| Organic matter (mould) . . . | 1 lb. to 70 lb. |
| Clay . . . . . | 5 lb. to 35 lb. |
| Sand . . . . . | 20 lb. to 90 lb. |
| Calcareous marl . . . . | 5 lb. to 20 lb. |

Soils fulfil the mechanical part of absorbing the moisture and heat from the atmosphere, and from their texture they admit the circulation of air to provide the necessary oxygen for the germination of the seed. They are the medium which admits the roots of the plant and hold it in position, and also they act the part of carriers by conveying the mineral nutriment, dissolved in the moisture they contain, to the roots.

The mineral constituents on which the fertility of a soil depends are confined to phosphoric acid, potash, nitrogen in the form of ammonia, and, to a lesser extent, lime. Their absence indicates a barren or exhausted soil, incapable of fertility without replenishment. To quote the words of a leading American agriculturist: "The farmer raises no crops which does not contain them, he sells no animal or vegetable

product which does not take them from his farm, and he has no soil so rich that they, or some of them, need not be returned to keep up its fertility. Whatever course of cultivation he pursues, he should never lose sight of these elements, and he should pay no greater heed to the dollars and cents that he receives and pays out than to the nitrogen, phosphoric acid, and potash which constitute his real available capital, and whose increase or decrease marks the rise and fall of his true wealth."

The texture of soils is also an important factor in their productiveness. They should be loose, and yet not light enough to become easily dry, nor should they be so heavy as to excessively retain the water during rainy weather.

The capacity of soils for water varies according to their character—a sandy soil will only absorb 24 per cent. of its weight before saturation occurs; a calcareous soil, 28 per cent.; a clayey loam, 47 per cent.; and a peaty soil, 80 per cent. A soil of this nature would require constant drainage to be of any agricultural use.

*Germination.*—Plants are derived from a germ contained within the seed. The seed is composed of a husk or frame enclosing the germ, with a storage of food to nourish it until it bursts forth with root and leaf. The food varies according to the character of the plant to come forth; with cereals it is starch, and in oil seeds, like mustard, linseed, rape, etc., it is fat. Potash and phosphoric acid form the mineral ingredients. Under ordinary circumstances the germ is dormant, but, surrounded with the favourable conditions of the soil, the seed swells, oxidation of the starch and fatty matter takes place, heat is developed within by the chemical action, and there results certain combinations by which the germ is nourished and grows, putting forth tiny rootlets and rearing a tender stem through the soil, whence commences the functions of plant life.

## Plant Life.

Plants are composed of water, carbon, oxygen, nitrogen, hydrogen, and sulphur, along with the mineral ingredients forming the ash when the plant is burnt. By far the largest proportion of growing plants is made up of water, then follow, according to their respective amounts, carbon, oxygen and sulphur, hydrogen and nitrogen. These elements unite amongst themselves, forming the starch, sugar, fat, alkaloids, and albuminoids present in the plants.

The composition of a growing plant (meadow grass) is given as follows :—

| | Parts per 100. |
|---|---|
| Water | 74·83 |
| Carbon | 11·74 |
| Hydrogen | 1·28 |
| Nitrogen | ·43 |
| Oxygen | 9·67 |
| Sulphur | ·19 |
| Ash | 1·86 |

The carbon is derived from the decomposition of the carbonic acid of the atmosphere; the oxygen and hydrogen are obtained from the water forming, in conjunction with carbon, the starch, sugar, and fat of the plant; the nitrogen is assimilated by the roots from the nitrogenous matter supplied to the soil; and the sulphur is a derivative of the sulphates from the soil also. If we eliminate the natural water we find the plant to be composed of 90 per cent. of matter taken from the atmosphere in the form of carbonic acid and moisture, with 10 per cent. of nitrogen and mineral ingredients abstracted from the soil.

It is thus seen that the atmosphere plays the most important part in the growth of the plant, and this atmospheric action is mainly carried on by the agency of the leaves. In the structure of a plant we have the stem, leaves, and roots. Through the roots are absorbed all the mineral

and nitrogenous matters and moisture; the stem acts as a carrier and support; while the leaves form the most important organs of the plant.

Man inhales the oxygen of the atmosphere, which is transformed by the wasting tissues of the body into carbonic acid, a poisonous gas, which he exhales. If no means were provided to break up into its constituents, carbon and oxygen, the carbonic acid so formed, the air would become surcharged with it, and human life would cease to exist. Nature, however, steps in and provides a remedy. The growing plant, through the leaves, decomposes the noxious gas by the aid of a green colouring matter (chlorophyll) contained within their cells, the carbon is absorbed through small openings in the leaves termed stomato, and goes to build up, by chemical union with the oxygen, hydrogen, and nitrogen, the carbo-hydrates and albuminoids essential for the growth of the plant.

The mechanical and chemical actions performed by the plant may be summarised as follows:—

(1) The absorption by the roots of the mineral ingredients and moisture;

(2) The decomposition of the atmospheric carbonic acid into carbon and oxygen by the chlorophyll of the leaves and their assimilation of the carbon;

(3) The combination of the carbon with the elements of water to form starch;

(4) The conversion of the starch into sugar, cellulose, and other carbo-hydrates;

(5) The action of nitrogen absorbed by the roots, as ammonia or nitrate, on the carbo-hydrates, and their conversion into amines and alkaloids, as glutamine, quinine, and brucine; and

(6) Their further change, by the action of sulphur, into that most important series of compounds termed albuminoids.

## CHAPTER VI.

### Natural Manures.

Manures may be divided into two broad classes—

(1) Natural manures.
(2) Artificial manures.

In the former we include all farmyard manures, litter, human excrementitious matter, and all those raw animal and vegetable products which reach the farmer, and are used for the small proportions of ammonia, phosphoric acid, and potash they contain. In the latter are embraced all the phosphatic manures, whether in the natural state as bones, rock phosphates, guanos, or manufactured as superphosphates, and prepared nitrogenous matters, special mixed manures, and mineral manures, as gypsum, common salt, kainite, marls, etc.

### Natural Manures.

The most important of all the natural manures is the farmyard manure. It is a mixture of solid and liquid excrementitious matter with straw and other vegetable remains, the solid matter holding the mineral ingredients of the food partaken by the animal, and in the urine or liquid portion the larger portion of the nitrogen existing as ammonia is found. In the following table the amounts of water and nitrogen held by farmyard and other nitrogenous manures are given :—

| Manure. | Water per cent. | Nitrogen per cent. Dry. | Wet. |
|---|---|---|---|
| Solid cow dung | 85·9 | 2·30 | 0·32 |
| Urine of cows | 83·3 | 3·80 | 0·44 |
| Solid horse dung | 75·3 | 2·21 | 0·55 |
| Horse urine | 79·1 | 12·50 | 2·61 |
| Sheep dung | 63·0 | 2·99 | 1·11 |
| Human excrements | 86·0 | 6·00 | 0·71 |
| Guano | 19·6 | 6·20 | 5·00 |
| Fresh bones | 25·0 | ... | 5·31 |
| Horn shavings | 9·0 | 15·78 | 14·39 |
| Coal soot | 15·6 | 1·59 | 1·35 |
| Wood soot | 15·6 | 1·31 | 1·15 |

Dr. Anderson gives the analysis of a farmyard manure of a mixed nature as follows:—

| | |
|---|---|
| Water | 72·48 |
| Organic matter | 13·94 |
| (Containing nitrogen, 0·38.) | |
| Potash | 0·32 |
| Soda | 0·16 |
| Lime | 0·59 |
| Magnesia | 0·02 |
| Phosphoric acid | 0·31 |
| Sulphuric acid | 0·12 |
| Carbonic acid | 0·52 |
| Ferric oxide and alumina | 0·45 |
| Sand | 11·09 |
| | 100·00 |

These analyses show that a farmyard manure contains only a small proportion of those nutritive ingredients necessary for the growth of the plant, and that its use alone on an impoverished soil will not restore that fertility on which depends the successful raising of a crop.

For restorative purposes, farmyard manure should be used in conjunction with "artificials" on a poor soil. It differs in its action according to its origin. Pig, sheep, and cow dung

decompose slower than horse dung, and, of the four, cow dung is the least valuable, from its lower percentage of nutritives.

Farmyard manure exercises a mechanical action on the soil, making it light and porous. For all crops, a compost with bone dust or guano, or, in many cases, with wood ashes and lime, acts very beneficially on the soil, yielding excellent results in the weight of crop.

The quantities used for different crops vary—

| | | | |
|---|---|---|---|
| Mangels consume about | 20 | tons per acre. | |
| Peas and beans | „ | 18 | „ |
| Wheat | „ | 12 | „ |

Naturally the effect of these quantities are in proportion to the composition of the soil. Human excrementitious matter is another manure of the same class.

By the adoption of the water-closet system in large towns, vast quantities of liquid and solid matter are produced; the solid matter is separated by gravitation, and the liquid portion is treated with alumino-ferric or other chemicals, the precipitate formed carrying with it the valuable phosphoric acid as phosphates of alumina and iron and potash and ammonia salts. The "sludge" formed is pressed, partly dried, and sold for manurial purposes.

It has been urged that the herbage from the use of such a manure is rank and harsh, and that it engenders the spread of parasitic diseases.

The following is an analysis of sewage manure:—

| | |
|---|---|
| Moisture | 10·95 |
| Organic matter | 38·71 |
| (Containing nitrogen, 3·06.) | |
| Lime | 5·47 |
| Oxides of iron and alumina | 6·19 |
| Alkaline salts | 5·62 |
| Phosphoric acid | 4·63 |
| Sand | 25·22 |
| | 99·79 |

The tops of all root crops, and marine vegetable products like seaweed, also form a very fair manure when ploughed in the soil. Time, however, is required for decomposition and yielding up of their mineral constituents. Dr. Griffiths enumerates their value as follows:—

"(1) They bring up plant food from the subsoil.

"(2) They increase the nitrogenous constituents in the surface soil.

"(3) As decomposition proceeds, carbonic acid is formed, which produces a disintegrating action upon the soil, thus converting some of the insoluble mineral constituents into soluble constituents.

"(4) They warm the land, and add to its power of retaining moisture and ammonia.

"(5) They promote the fertility of heavy clays by rendering them less sticky or adhesive."

## CHAPTER VII.

### Artificial Manures—Raw and other Phosphates.

### Bones.

*Raw Bones.* — Raw bones rarely enter the farmyard. They are unsuitable for spreading on land, and their action, in yielding up the phosphoric acid and nitrogen (existing as insoluble phosphate and gelatinous matter) to the soil is very slow. In the state as received from the marine store dealers, butchers, and abattoirs, the farmer would pay for a heavy percentage of fat and moisture, which is of no manurial value; all the phosphates would be in an insoluble form, and he would require a mill driven by steam power to break or crush the bones into half-inch or quarter-inch size, as may be desired. To reduce to a fine state of division, and form a friable mass for the drill, is not possible, for the crushed bones would assume a pasty form from the organic matters and moisture present. Bone dealers do not, as a rule, sell to farmers, but treat direct with the fat, glue, and manure manufacturers, and it is the latter, after extracting the fatty and gelatinous matters, that sell to the farmer the residual bones, either as crushed, ground to bone meal, or in the form of soluble superphosphates.

Regarding the supply of home bones, it may be remarked that they are not equal to the demand, consequently manufacturers are compelled to fall back on supplies from South America, Russia, India, and other countries. Foreign bones are all partially degreased and degelatinised by boiling or steaming before being exported. Raw bones of home supply

contain fat, organic and gelatinous matters, and mineral ingredients, as phosphate of lime, carbonate of lime, and a small proportion of alkaline salts. Now the fat, which averages 12½ per cent. of the raw bone, has no manurial value, yet it is worth £20 per ton for glycerine, candle, and soap-making; the organic matter, which is valuable only to the farmer for the 3½ to 4 per cent. of nitrogen, yields the glue of commerce, with a value of £28 to £32 per ton, according to quality. In taking out these products, the bones undergo no deterioration, except a lowering of the percentage of nitrogen; on the other hand, the phosphates are increased from the elimination of the fat and gelatinous matter, the moisture is less by one-half, and the bones are left in a condition to be crushed to any desired size, or ground to a fine meal, and thus more easily assimilated by the soil. The nitrogen is lowered to 1 to 2 per cent., according to the methods of extraction employed.

The following two analyses by the author, shows the chemical value of raw bones. The samples were taken as an average of the raw bones coming into the works on two different occasions:—

| | | |
|---|---|---|
| Moisture . . . | 20·46 | 17·67 |
| Organic matter [1] . . | 34·09 | 33·84 |
| Phosphate of lime . | 39·21 | 42·15 |
| Carbonate of lime . | 4·16 | 3·52 |
| Alkaline salts . . | 1·14 | 1·76 |
| Sand (silica) . . | ·94 | 1·06 |
| | 100·00 | 100·00 |
| [1] Containing nitrogen = . | 3·63 | = 3·52 |

Taking the average, these analyses show that the constituents of any value for manurial purposes are—

| | | |
|---|---|---|
| Nitrogen . | 3·57 per cent. | = 49·54 per cent. |
| Phosphate of lime | 40·68 ,, | |
| Carbonate of lime | 3·84 ,, | |
| Alkaline salts | 1·45 ,, | |

and that, if the raw bones could be reduced to a state of fineness as to be suitable to the farmer, he would still be paying for 50 per cent. of material and moisture of no value to the soil, yet of great commercial importance as glue and fat. Bones, as received in the farmyard, are half-inch, quarter-inch, or ground into bone meal. They are degreased and degelatinised, either by the benzene process, or by boiling in open pans, or steaming under pressure. If the benzene process is adopted, and a good system of glue extraction followed, then the treated bones, from their friable and porous nature, form an excellent bone meal to the farmer, although low in nitrogen; but as he buys on the unit strength of nitrogen present, he suffers no monetary loss with the low percentage; on the other hand, the phosphates are high, running 60 to 62 per cent. of tribasic phosphate, and are physically in a better condition to be absorbed by the soil. They have, however, not the same value as dissolved bones, with the same percentage of phosphate, rendered more or less soluble by treatment with an acid.

The following two analyses made by the author show the composition of bone meal from bones treated by the benzene process and then degelatinised:—

| | (1) | (2) |
|---|---|---|
| Moisture . . . | 9·25 | 8·54 |
| Organic matter[1] . . | 17·66 | 19·53 |
| Phosphate of lime . . | 62·39 | 61·22 |
| Magnesia and carbonate of lime . . . | 8·55 | 8·74 |
| Alkaline salts . . | ·38 | ·59 |
| Silicious matter . . | 1·77 | 1·38 |
| | 100·00 | 100·00 |
| [1] Containing nitrogen . | ·97 per cent. | 1·05 per cent. |
| Equal to ammonia . | 1·17 ,, | 1·27 ,, |

In raising the nitrogen 1 or 2 per cent. a good organic nitro-

genous material intimately mixed with bulk in the required proportions will serve the purpose, and not in the least alter the nature of the meal.

*Boiled and Steamed Bones.*—In bones that have been boiled or steamed, the extraction of the fatty and gelatinous matters is not so economical as that by the benzene process; the yield of fat and glue being lower, that portion of the latter left in the bone increases the nitrogen 1 to 2 per cent. Against this may be placed a lower percentage of phosphates, and a meal not considered equal to that produced from bones treated with benzene.

The following are two analyses, by the author, of boiled and steamed bones:—

| | Boiled Bones. | Steamed Bones. |
|---|---|---|
| Moisture | 10·81 | 10·79 |
| Organic matter [1] | 25·97 | 22·48 |
| Phosphate of lime | 53·15 | 57·17 |
| Magnesia and carbonate of lime | 6·28 | 6·89 |
| Oxide of iron | ·27 | Trace. |
| Alkaline salts | 1·07 | ·86 |
| Sand (silica) | 2·45 | 1·74 |
| | 100·00 | 99·93 |
| [1] Containing nitrogen | 1·91 per cent. | 1·64 per cent. |
| Equal to ammonia | 2 31 ,, | 1·99 ,, |

Adulteration of bone meal is still practised, but not on so large a scale as formerly. The author recently tested a sample of material used by a firm for mixing with meal, and found it to contain 90 per cent. of sand.

*Bone Ash.*—On calcining a raw bone, a white or yellowish white product is obtained, having the shape of the original bone. This is the bone ash of commerce, and chiefly imported from South America. It has a limited use in the manufacture of superphosphates. Some samples under the author's notice have tested as high as 88·43 per

cent. of tricalcium phosphates, others again have been poor, with 70 per cent. Bone ash does not contain any nitrogen. A use for considerable quantities of bone ash of good quality is found in the manufacture of substitutes for cream of tartar for plain and fancy baking. The bone ash is treated with certain proportions of good quality sulphuric and phosphoric acids to give the necessary acidity. The "acided" product is then dried, ground to a fine powder, and mixed with flour to give bulk. The composition is sold under different names, and its strength is based on the number of c.c.'s of a decinormal alkali required to neutralise it.

*Bone Charcoal.* — Bone charcoal depends for its decolorising power on the chemical attraction proceeding from its surface, and which absorbs the colouring matter of the liquids passed through it. In course of time this attraction gradually weakens, and is ultimately destroyed. The char in this state is called "spent," and is of no further use to the sugar refiner. Containing a high percentage of phosphates, it is readily bought up by the manure manufacturer at £2, 5s. to £2, 10s. per ton, and from its condition it is easily worked with sulphuric acid, forming an excellent high-grade superphosphate. Samples of Leith, Liverpool, and Greenock spent chars, examined by the author, gave respectively—

72·21 per cent. tribasic phosphate.
70·24 „ „ „
74·00 „ „ „

The following is an average analysis of "spent" char:—

| | |
|---|---|
| Carbon (nitrogenous) . . . | 20·65 |
| Phosphate of lime . . | 70·58 |
| Carbonate of lime . . . . | 5·17 |
| Sulphate of lime . . . . | ·26 |
| Oxide of iron . . . . | ·76 |
| Sand (silica) . . . . | 2·57 |
| | 99·99 |

## Mineral Phosphates.

In the manufacture of superphosphates large quantities of rock or mineral phosphates are used in addition to the bone phosphates above described. Their unit value, however, is lower than that of a bone phosphate. The presence also of considerable amounts of the oxides of iron and alumina, carbonate and fluoride of calcium, lessens their worth.

Mineral phosphates are never used alone, but in the state of superphosphates, a proportion of their phosphates being rendered soluble by treatment in a finely powdered condition with sulphuric acid. They are "mined" in many parts of the globe, and may be briefly described as—

(1) *Canadian Phosphates.*—The Canadian phosphates, when pure, may be considered as a true apatite, being a definite combination of phosphate of lime and fluoride of calcium with the formula of $9CaO{\cdot}3P_2O_5 + CaFl_2$.

Canadian apatite is considered one of the best of mineral phosphates for the preparation of superphosphates, from the high percentage of phosphate of lime it contains. The following three analyses by Dr. Voelcker express the composition of apatite :—

| | (1) | (2) | (3) |
|---|---|---|---|
| Moisture, water of combination, and loss on ignition . . . . | ·62 | ·10 | ·11 |
| Phosphoric acid[1] . . . . | 33·51 | 41·54 | 37·68 |
| Lime[2] . . . . . | 46·14 | 54·74 | 51·04 |
| Oxides of iron and alumina, and fluorine, | 7·83 | 3·03 | 6·88 |
| Silica . . . . . | 11·90 | ·59 | 4·29 |
| | 100·00 | 100·00 | 100·00 |
| [1] Equivalent to tribasic phosphate of lime . | 73·15 | 90·68 | 82·85 |
| [2] Excess of lime over the amount required to form tribasic phosphate . . . . | 6·50 | 5·60 | 6·47 |

The excess of acid is a guide to the economical working of a mineral phosphate: the higher the excess the greater the amount of acid necessary to work up the mineral, and thus more costly is the superphosphate produced.

Canadian apatite occurs in distinct crystalline masses of a light green, and sometimes of a reddish tint, and is found in the Laurentian rocks of what the geologists term the Palæozoic age. Undoubtedly the heavy freight to ports of the United Kingdom check any extensive use of this valuable phosphate.

(2) *Norwegian Apatite.*—It is closely allied with the Canadian deposit, the tricalcium phosphate being combined with calcium chloride, the mineral being classed as a chlor-apatite. For certain reasons, little is used in this country, but it forms a valuable source of phosphate for manure-making. Samples of the mineral show 76 to 80 per cent. of phosphates, with very little of the oxides of iron and alumina.

(3) *South Carolina Land and River Phosphates.*—These phosphates, along with a similar class from Florida, are largely exported to England. The land phosphates, in the form of nodules, are mined round Charlestown. To some extent they are fossiliferous, and are of a light yellow or brown colour, according to the oxide of iron present. The river phosphates are dredged all the year round by large "bucket" dredgers working on the Savannah, Saluda, and other rivers; on raising they are well washed of sand, dried, and exported. The river phosphates are very dark in colour, and much harder than the "land" quality. From the proceedings of the Royal Agricultural Society the following four analyses are taken as representing the average composition of these phosphates:—

*Land Phosphates.*

| | (1) | (2) |
|---|---|---|
| Water and water of combination | 7·40 | 2·29 |
| Phosphoric acid [1] | 26·50 | 24·29 |
| Lime | 37·20 | 38·71 |
| Oxides of iron, alumina, magnesia, and carbonic acid | 16·27 | 17·28 |
| Silica | 12·63 | 17·43 |
| | 100·00 | 100·00 |
| [1] Equivalent to tribasic phosphate of lime | 57·85 | 53·02 |

*River Phosphates.*

| | (3) | (4) |
|---|---|---|
| Water, water of combination, and loss on ignition | 4·07 | 1·56 |
| Phosphoric acid [1] | 28·44 | 26·89 |
| Lime | 45·07 | 42·28 |
| Magnesia, oxides of iron and alumina, carbonic acid | 15·16 | 18·47 |
| Silica | 7·26 | 10·80 |
| | 100·00 | 100·00 |
| [1] Equivalent to tribasic phosphate of lime | 62·09 | 58·70 |

On comparing the phosphate of lime in these analyses, it will be noticed that the "river" has a higher percentage than the "land" phosphate, and consequently is of more value.

(4) *Navassa Phosphates.*—These are obtained from the island of Navassa in the Caribbean Sea, and exist in the form of nodules of a reddish brown colour. They contain a high percentage of phosphate of lime, and are well adapted for the manufacture of superphosphates. The limited production, high working charges, freightage, etc., makes at present their shipment to this country unremunerative. Their composition is seen from the following two analyses of cargo samples:—

| | (1) | (2) |
|---|---|---|
| Water and combined water . . | 12·08 | 10·90 |
| Phosphoric acid [1] . . . . | 30·21 | 31·08 |
| Lime, . . . . . | 35·32 | 36·54 |
| Magnesia, carbonic acid, oxide of iron, alumina . . . | 19·65 | 17·78 |
| Silica (sand) . . . . . | 2·74 | 3·70 |
| | 100·00 | 100·00 |
| [1] Equivalent to tribasic phosphate of lime . . . . . | 65·94 | 67·85 |

(5) *Sombrero Phosphates.*—These phosphates, from the island of Sombrero, in the group of the Leeward Islands in the Caribbean Sea, are practically exhausted. They were of high quality, and averaged 70 per cent. of tri-calcic phosphate.

(6) *Aruba Phosphates.*—Infrequently cargoes are found in the market of this class of mineral phosphates. Although rich in phosphates, the presence of considerable quantities of carbonate of lime and oxide of iron and alumina detracts from their value. The phosphate of lime averages 72 per cent.

(7) Other West Indian islands produce to a limited extent mineral phosphates of varied composition, Maracaibo phosphate, from the island of that name, yielding the highest percentage of phosphate of lime (average 78 per cent.), with low amounts of oxide of iron and alumina. Maracaibo mineral forms an excellent superphosphate. The small islands of Redonda and Alta Vela, in the West Indian group, yield a mineral phosphate in which the lime is replaced by alumina and ferric oxide, forming phosphates of alumina and iron. Through the want of lime, the mineral cannot be employed in the manufacture of superphosphates. Samples of Redonda and Alta Vela phosphates show respectively 70 and 50 per cent. of iron and alumina phosphates. Their

agricultural value is considered low, although a leading authority says, from his own experience, that good crops can be got with the use of Redonda in a fine state of division. Various countries in Europe produce large quantities of mineral phosphates, distinguished as coprolites, phosphorites, etc. Some are valuable from the high yields of phosphate, and the presence of but moderate quantities of carbonate of lime, iron, and alumina. Others again are low in phosphates, heavily impregnated with iron, and hardly worth the cost of exporting.

### English Coprolites.

English coprolites are found in Cambridgeshire, Suffolk, Norfolk, and Bedfordshire; the finer qualities are furnished by the first-named county, from the Upper Greensands, and are of a grey colour. They are largely used, and well suited for the manufacture of superphosphates. The following analyses represent their composition:—

| | (1) | (2) |
|---|---|---|
| Water | 2·30 | 3·79 |
| Water of combination | 1·50 | |
| Phosphoric acid[1] | 26·05 | 29·14 |
| Lime | 43·68 | 45·05 |
| Oxide of iron and alumina | 18·70 | 19·68 |
| Silica | 7·77 | 2·34 |
| | 100·00 | 100·00 |
| [1] Equivalent to tribasic phosphate of lime | 56·87 | 63·60 |

*Suffolk Coprolites.*—Suffolk coprolites are of a brown colour, and somewhat inferior to the Cambridge phosphate. They contain from 48 to 52 per cent. of calcium phosphate with 14 to 16 per cent. of carbonate of lime. The superphosphate formed from their use is lower in quality than that made from Cambridge phosphate.

*Bedfordshire Coprolites.*—These coprolites may be classed

with the Suffolk phosphate. They are also of a brown colour, and contain—

| | |
|---|---|
| Moisture and water of combination | 3·35 |
| Phosphoric acid [1] | 23·47 |
| Lime | 36·29 |
| Ferric oxide | 5·39 |
| Alumina, magnesia, and fluorine | 7·24 |
| Carbonic acid | 3·45 |
| Silica | 20·81 |
| | 100·00 |
| [1] Equivalent to tribasic phosphate of lime | 51·24 |

*French Phosphorites.*—The richest mineral deposits of France are those mined at Loire and Garonne, and known in this country as French or Bordeaux phosphates. They have a yellowish brown colour, and are very hard. With sulphuric acid they are readily dissolved, and form high-grade superphosphates. The following two analyses are representative of their composition—

| | (1) | (2) |
|---|---|---|
| Water | 2·60 | ·89 |
| Water of combination | 2·62 | 2·58 |
| Phosphoric acid [1] | 34·46 | 31·50 |
| Lime | 46·11 | 41·12 |
| Oxide of iron<br>Alumina and carbonic acid | 10·77 | 13·73 |
| Silica | 3·44 | 10·18 |
| | 100·00 | 100·00 |
| [1] Equivalent to tribasic phosphate of lime | 75·23 | 68·76 |

Around Bologne there exists phosphatic deposits, having an appearance and chemical composition similar to the inferior qualities of our own coprolites. They have but a limited use in this country for the manufacture of low-grade superphosphates. The calcium phosphates they contain averages about 43 per cent.

*Belgian Phosphates.* — These deposits exist in a fine powdery condition, and after washing and drying are brought up to a strength of about 46 to 47 per cent. of phosphate. They are not used alone, but in conjunction with high-grade phosphates. The addition improves the porosity and dryness of a superphosphate.

*German Phosphates.*—The best known and probably the most extensive deposits of German phosphates are found near the river Lahn below Weelbach, and to which the name of Nassau is given.

Some samples, representing limited quantities, test as high as 75 per cent. phosphate, but the bulk is of low quality, and found mixed with varying proportions of clay, limestone, ironstone, phosphate of alumina, etc. The importations to this country are not now of any importance. The phosphate averages about 50 per cent.

*Spanish Phosphorites.*—Spain supplies a large quantity of rich phosphates, mined in the province of Estramadura. They are of a light yellow colour, with a crystalline structure, and belong to the class of fluor-apatites. The following table shows their composition :—

| | From Caceres. | From Montanchez. |
|---|---|---|
| Water | ·21 | ·16 |
| Phosphoric acid [1] | 38·85 | 39·09 |
| Lime | 51·65 | 51·77 |
| Fluorine, carbonic acid, and a little oxide of iron | 2·61 | 3·02 |
| Silica (quartz rock) | 6·88 | 5·91 |
| | 100·00 | 100·00 |
| [1] Equivalent to tribasic phosphate of lime | 84·33 | 85·33 |

In the manufacture of "basic" steel, a residual slag or cinder is produced, containing on an average about 15 per cent. of phosphoric acid, with 20 to 22 per cent. of iron

as ferrous and ferric oxides. It has been found that a large proportion of this phosphoric acid (existing as phosphate of iron) is readily soluble in weak acid solutions, and thus made available for agricultural purposes. According to Dr. Wagner, the cinder is well adapted for moss and peaty meadow soils when ploughed well in; and the same authority advocates its use as a manure for oats, wheat, barley, and flax, about 3 cwt. per acre being used.

In successfully using the "Thomas cinder," it must be ground to an impalpable powder to enable absorption into the roots.

Notwithstanding the excellent virtues attributed to its use by German agricultural authorities, the consumption in this country (which produces over 100,000 tons of the cinder a year) is not great, farmers generally taking an unfavourable view of its fertilising value, some remarking that its action is harsh, and that after a time the soil becomes "burnt."

*Guanos.*—The guanos of commerce may be divided into—

GUANOS.

(1) Guanos proper;
(2) Guano phosphates.

Guanos proper are the rich excrementitious matter of sea-birds found on the Peruvian coast. They have undergone little decomposition by the action of tropical rains, and consist of uric acid, urate of ammonia, with proportions of phosphate of lime and ammonia, sulphates and chlorides of potash, and soda, and silicious matter; the nitrogenous portion consisting of two-thirds, and the mineral matter one-third of the whole,—the nitrogen equivalent being from 17 to 19 per cent. All guanos at some early period have been very rich in nitrogen, but through the action of rain

and other atmospheric influences have undergone, to some extent, a change, the water converting the urates into volatile carbonate of ammonia and other soluble ammoniacal salts. When the watery action is prolonged, nearly, if not the whole, of these ammonia compounds are removed by solution, the deposits becoming mainly phosphates with 1 to 2 per cent. of nitrogen, and are known as guano-phosphates. Guanos are a complete manure in themselves, containing all the necessary fertilising ingredients in the form of soluble ammonia salts, phosphoric acid, and potash. They can be used with success on either heavy or light soils of a clayey or sandy nature, forming an excellent admixture for nearly all crops.

Guanos are now sold on the unit of nitrogen they contain, and thus the farmer is protected from any adulteration, formerly practised to a large extent. If he buys with 17 to 18 per cent. nitrogen or as low as 1 to 2 per cent., he pays accordingly. It is to his interest, however, that the certificate of analysis should guarantee the sample as a true average of the bulk, and not one selected for its richness.

As is well known, guanos, especially when moist, emit a strong, pungent, ammoniacal odour, due to the volatilisation of carbonate of ammonia, and on standing for any length of time this loss becomes a serious one. To fix this ammonia and render the guanos in a dry and friable condition and easily worked with the drill, many manure manufacturers now treat them with strong sulphuric acid in the mixing trough of the manure shed, the action fixing all the ammoniacal compounds as a soluble sulphate of ammonia, renders the phosphates they contain largely soluble, and produces a powdery guano liable to no further change by exposure. In such a form the guanos are a quick-acting manure, and contain 20 to 23 per cent. of soluble phosphates, with about nine per cent. of ammonia. In the mixing, the ammonia can

be enriched in the guano by the addition of dried blood or sulphate of ammonia, as may be desired.

The following is a description of the leading guanos and guano-phosphates that have been, or are presently used, for agricultural purposes:—

(1) *Angamos Island Guano.*—From the island of Angamos, off the Peruvian coast, a rich, dry excrement is imported into this country. It is of a light yellow colour, and contains 19 to 21 per cent. of nitrogen, with 12 to 13 per cent. of phosphates, partly soluble. The following two analyses represent its composition:—

| | (1) | (2) |
|---|---|---|
| Moisture . . . . . | 7·24 | 8·76 |
| [1] Organic matter and salts of ammonia | 69·01 | 69 96 |
| Phosphates of lime and magnesia . | 12·06 | 12·07 |
| Alkaline salts . . . . . | 9·02 | 8·27 |
| Silica . . . . . | 2·67 | ·94 |
| | 100·00 | 100·00 |
| [1] Containing nitrogen . . . . | 21·15 | 19·30 |

(2) From the Peruvian islands of Chencha, Guanape, and Ballestas, considerable quantities of a fairly rich Peruvian guano have been exported at different times. They contained—

| | Chencha Islands. | Guanape Island. | Ballestas Islands. |
|---|---|---|---|
| Water. . . . . | 13·67 | 17·79 | 19·19 |
| [1] Organic matter and ammonia salts | 52·05 | 42·62 | 48·19 |
| Calcium and earthy phosphates . | 22·78 | 25·45 | 20·69 |
| Alkaline salts . . . . . | 9·67 | 11·92 | 9·40 |
| Sand . . . . . | 1·83 | 2·22 | 2·53 |
| | 100·00 | 100·00 | 100·00 |
| [1] Containing nitrogen . . . | 13·61 | 10·04 | 13·60 |

(3) *Pabillon de Pica Guano.*—This group of Peruvian islands export a rich guano, very dry, and of a reddish yellow colour. A sample, on analysis by the author, gave—

| | |
|---|---|
| Moisture | 2·35 |
| [1] Organic matter and salts of ammonia, by ignition | 63·75 |
| Phosphoric acid | 9·09 |
| Lime | 10·14 |
| Magnesia | 2·65 |
| Ferric oxide | Trace |
| Alkaline salts | 7·38 |
| Silica | 4·64 |
| | 100·00 |
| [1] Containing nitrogen | 17·03 |

(4) *Ichaboe Guano.*—From the Ichaboe Islands, on the south-west coast of Africa, we import a moderate quantity of a rich guano. A sample, on analysis by the author, had the following composition :—

| | |
|---|---|
| Moisture | 12·28 |
| [1] Organic matter and salts of ammonia, by ignition | 51·25 |
| Phosphoric acid | 12·09 |
| Lime | 12·25 |
| Magnesia | 1·06 |
| Alkaline salts | 4·83 |
| Silica | 6·24 |
| | 100·00 |
| [1] Containing nitrogen | 14·22 |

*Guano-Phosphates.*—The guano-phosphates are distributed over a wide area, being found in Bolivia, Peru, and as far south as the Falkland Islands and Patagonia; they exist also in considerable quantities in some of the West Indian islands, the Gulf of California, and South Africa. They contain from 1 to 2 per cent. of nitrogen, with varying proportions of phosphates. The guano-phosphates have a reddish yellow

colour, and are generally found in a powdery condition. As before mentioned, these phosphates were originally rich guano deposits, which at different periods have been subjected to a heavy rainfall, resulting in the decomposition of the nitrogenous matter and the washing out of the larger portion of the soluble ammonia salts formed.

They are mainly used for the manufacture of "dissolved guano," the nitrogen being enriched by the addition of dried blood or sulphate of ammonia, and for the manufacture of superphosphates for special manures.

Guano-phosphates, from their deficiency in nitrogen, have a lower value than the guanos proper.

The following are the chief guano-phosphates that are used for manufacturing purposes:—

(1) *Megillones Guano-Phosphate.*—This guano-phosphate is found on the high tableland near the Bolivian coast. It has a bright red colour and occurs as a powder. The nitrogen is low and the phosphates partly soluble.

Dr. Voelcker gives the composition of two cargo samples as follows:—

| | (1) | (2) |
|---|---|---|
| Moisture | 8·76 | 7·45 |
| [1] Organic matter and salts of ammonia | 6·49 | 7·34 |
| Phosphoric acid [2] | 34·40 | 30·72 |
| Lime | 37·60 | 36·81 |
| Ferric oxide | ·54 | ·38 |
| Magnesia | 2·83 | 8·56 |
| Alkaline salts | 5·76 | |
| Carbonic acid | ·45 | ·75 |
| Sulphuric acid | 1·68 | 6·76 |
| Silica | 1·49 | 1·23 |
| | 100·00 | 100·00 |
| [1] Containing nitrogen | ·98 | ·89 |
| Equivalent to ammonia | 1·19 | 1·08 |
| Equivalent to tribasic phosphate of lime | 75·09 | 64·06 |

From its high percentage of phosphates, with their quota in the soluble form, and from the dry and powdery condition, this phosphate forms a good manure when used alone or dissolved with acid. For some crops it is considered equal to Chili saltpetre.

(2) *Curacoa Guano-Phosphate.*—This phosphate from Curacoa Island, South America, is an example of guano from which the whole of the ammoniacal matters have been washed out by the prolonged action of water. It may be classed as a phosphate and carbonate of lime mixed with alkaline sulphates and silicates, and from its high phosphatic strength is found very suitable for the manufacture of superphosphates.

From a sample, the author found—

| | |
|---|---|
| Moisture | 9·33 |
| Organic matter | 4·28 |
| Phosphoric acid | 34·83 |
| Lime | 42·21 |
| Carbonic acid | 3·05 |
| Magnesia | ·59 |
| Potassium and sodium sulphates | 3·25 |
| Sodium chloride | 1·57 |
| Silica | ·89 |
| | 100·00 |

(3) *Falkland Islands Guano-Phosphates.*—The Falkland Islands supply a phosphate containing a fair proportion of ammoniacal salts. Unfortunately they are heavily charged with water, and have a strong pungent smell from the volatile ammonium carbonate. The phosphates are best treated with sulphuric acid, to fix the ammonia and render them dry and friable for use with the drill.

The following two analyses by Dr. Voelcker represent their composition:—

| | (1) | (2) |
|---|---|---|
| Moisture | 33·43 | 35·86 |
| [1] Organic matter and salts of ammonia | 21·42 | 26·07 |
| Phosphates of lime and magnesia | 32·04 | 22·01 |
| Carbonate of lime | 2·52 | 5·64 |
| Alkaline salts | 6·22 | 7·34 |
| Silica | 4·37 | 3·08 |
| | 100·00 | 100·00 |
| [1] Containing nitrogen | 4·31 | 4·42 |
| Equivalent to ammonia | 5·23 | 5·31 |

(4) *Raza Island Guano-Phosphate.*—From the Gulf of California is obtained a phosphatic guano of high strength, and with ½ to 1 per cent. of nitrogen. The deposit is very dry and powdery, and has a reddish yellow colour. It is a valuable addition to the manure shed for superphosphate-making. The following two cargo samples illustrate its value for manurial purposes:—

| | (1) | (2) |
|---|---|---|
| Water | 4·83 | 1·30 |
| Organic matter [1] and combined water | 12·72 | 9·80 |
| Phosphoric acid [2] | 34·33 | 40·31 |
| Lime | 37·36 | 37·21 |
| Magnesia | 1·76 | |
| Ferric oxide | ·50 | |
| Alumina | ·81 | 7·18 |
| Carbonic acid | ·46 | |
| Alkaline salts | 5·54 | |
| Silica | 1·69 | 4·20 |
| | 100·00 | 100·00 |
| [1] Containing nitrogen | 1·04 | ·37 |
| Equivalent to ammonia | 1·26 | ·45 |
| [2] Equivalent to tribasic phosphate of lime | 74·94 | 88·01 |

(5) *Baker Island Guano-Phosphate*—This deposit has a high strength of phosphate of lime, but contains little or no nitrogen. Like other guano-phosphates, it is well suited for treatment with sulphuric acid, being dry and in a fine condition. Its composition is seen from the following two analyses:—

| | (1) | (2) |
|---|---|---|
| Water | 12·05 | 4·71 |
| Organic matter [1] | 6·25 | 6·17 |
| Phosphoric acid [2] | 32·32 | 39·44 |
| Lime | 42·34 | 43·01 |
| Magnesia | 0·76 | 2·32 |
| Ferric oxide | 0·14 | |
| Alumina | 0·09 | 0·96 |
| Sulphuric acid | 1·19 | |
| Carbonic acid | 2·99 | 0·27 |
| Alkalies | 1·78 | 2·33 |
| Silica | 0·14 | 0·79 |
| | 100·00 | 100·00 |
| [1] Containing nitrogen | ... | 0·34 |
| Equivalent to ammonia | ... | 0·41 |
| [2] Equivalent to tribasic phosphate of lime | 70·55 | 86·11 |

(6) Other supplies are obtained from Patagonia, Sydney Island, Jarvis Island, Aves Island, and from Australia. All are practically a phosphate of lime with varying proportions (·25 to ·5) of nitrogen, and their value rests on their condition and the phosphate they contain. Like the other guano-phosphates that have been described, they are chiefly used for dissolving purposes.

## CHAPTER VIII.

### Mineral Manures.

### Sodium Chloride (Common Salt).

Common salt, or that quality described as agricultural salt, is now used in considerable quantities for manurial purposes.

Chemically speaking, it is a combination of the metal sodium with chlorine gas, the resulting compound being termed sodium chloride.

Geographically, it is distributed over a wide area, being found in practically inexhaustible quantities in the districts of Nantwich and Northwich in Cheshire, and Droitwich in Worcestershire; in the State of Michigan and other places of the American continent; in Russia, Germany, Austria, and Persia.

In England, salt is not mined, but the brine, which is a saturated solution of the salt, is pumped up from considerable depths of the earth's crust, designated by geologists as the Triassic period. The brine is evaporated in pans to form the different kinds of salt found in commerce, the finest quality of which is the domestic table salt.

The following table of analyses, as made by G. E. Cooke, give an idea of the composition of various samples taken from —1, Northwich (Cheshire); 2, Dreuze (Lorraine); 3, Droitwich (Worcestershire); 4, Goderich (Ontario); 5, Saginaw (Michigan, U.S.A.); 6, Nantwich (Cheshire).

| | (1) | (2) | (3) | (4) | (5) | (6) |
|---|---|---|---|---|---|---|
| Sodium chloride . | 96·36 | 97·59 | 96·93 | 97·03 | 92·97 | 90·23 |
| Calcium chloride . | ·01 | ... | ... | ·01 | 1·09 | ... |
| Magnesium chloride | ·02 | ... | ·02 | ·03 | ·50 | ... |
| Calcium sulphate . | 1·17 | 1·02 | 3·05 | 1·43 | ·33 | 1·68 |
| Carbonates of lime and magnesia . | ... | ... | ... | ... | ... | ·75 |
| Oxide of iron . | ... | ... | ... | ... | ... | ·87 |
| Sulphates of sodium and magnesia . | ... | ·80 | ... | ... | ... | ... |
| Insoluble matter . | ... | ... | ... | ... | ·01 | ... |
| Water . . . | 2·24 | ·50 | ... | 1·50 | 5·10 | 6·38 |
| | 99·80 | 99·91 | 100·00 | 100·00 | 100·00 | 100·00 |

Agricultural salt varies from 90 to 93 per cent. of sodium chloride, is rather moist, and contains a small proportion of iron.

Although formerly disputed, it is now recognised by agriculturists that salt is beneficial to the soil when applied in moderate quantities, either alone or in conjunction with sodium nitrate. Not only as a plant food is it valuable, but its action on the land is considerable, keeping it cool and moist, and destroying all soil vermin.

Johnstone, in his work on *Agricultural Chemistry* (1852), says salt "destroys small weeds, improves the quality of pastures, rendering them more palatable; strengthens and brightens the straw, and makes the grain heavier per bushel, both of wheat and oats. It has also been observed to produce specially good effects on mangold-wurtzels." Later, Liebig speaks a word in its favour. He says: "We have every reason to believe that where the crops are increased by manuring with common salt alone, or when the favourable influence of salts of ammonia or nitrate of soda is augmented by the addition of common salt, the operation of the three salts essentially depends upon their power of diffusing the nutritive substances present in the

soil or of preparing those substances for absorption"; and after quoting the results of some experiments carried out by the Bavarian Agricultural Society, continues: "In both these series of experiments the crops of corn and straw were remarkably increased by the addition of common salt." Professor Shelton, a leading American agriculturist, further shows its value in this respect on wheat. He writes: "A dressing of 300 lb. salt per acre on two plots gave an average increase of close on 9 per cent. of cleaned grain as compared with plots not dressed, as well as an increase of straw."

Common salt also plays a very important part in decomposing certain organic and inorganic constituents of the soil, rendering them soluble and in a fit state to be absorbed by the plant as food.

### Potash Salts.

*Kainite.*—The compounds of potassium used in agriculture are the sulphate and chloride. The sulphate of potash is never used in the pure form, but in combination with magnesium salts, forming the mineral kainite. This natural product is obtained from the celebrated mines of Stassfurt, in Germany, and exists as a sulphate of potash combined with chloride and sulphate of magnesia. Lime authorities state the formulæ to be $K_2Mg(So_4)_2$, $MgCl_2$, $6H_2O$. It has a yellowish grey colour, and effloresces in a dry atmosphere.

The following is an analysis of a sample of kainite by the author:—

| | |
|---|---|
| Total water, mechanical and in combination | 15·16 |
| Oxides of iron and alumina | ·34 |
| Sulphate of potash | 25·07 |
| Chloride of sodium | 20·51 |
| Chloride of magnesia | 18·13 |
| Sulphate of magnesia | 17·08 |
| Sulphate of lime | 2·29 |
| Insoluble matter | 1·42 |
| | 100·00 |

The sulphate of potash present is equal to 12·98 per cent. of potash ($K_2O$). Generally, kainite is not used alone, but in conjunction with superphosphates, guanos, and for many mixed manures, being one of the leading sources for enriching these manures with their potash food.

*Chloride of Potash.*—The chloride, or muriate of potash, as it is sometimes termed, is obtained from the carnellite deposits in the Stassfurt region. Carnellite is a combination of the chlorides of potash, soda, and magnesia with sulphate of magnesia and water of crystallisation. Dr. Thorpe gives the analysis of a sample of this mineral deposit as follows:—

| | |
|---|---|
| Chloride of potash | 15·7 |
| Chloride of sodium | 21·5 |
| Chloride of magnesia | 21·3 |
| Chloride of calcium | ·3 |
| Sulphate of magnesia | 13·0 |
| Insoluble matter | 2·0 |
| Water | 26·2 |
| | 100·0 |

The carnellite is crushed, boiled with water, and the chloride of potash crystallised out. By recrystallisation it is obtained in a very concentrated state, 98 to 99 per cent. Two analyses by the author of the commercial product, guaranteed 98 per cent. chloride, were as follows:—

| | (1) | (2) |
|---|---|---|
| Chloride of potash | 98·81 | 98·05 |
| Sodium chloride | ·38 | ·63 |
| Chloride of magnesia | ·26 | ·58 |
| Sulphate of magnesia | ·29 | ·36 |
| Insoluble matter | ·14 | ·38 |
| | 99·88 | 100·00 |

Many manure manufacturers use the chloride as a cheaper potash compound in the concentrated state than the kainite. Other sources of potash exist in suint, kelp, wood ashes, fish offal, etc.; the low percentage of potash, however, makes their use very limited. They cannot compete with the Stassfurt salts.

Potash salts, used as an admixture with phosphates, are recognised as excellent manuring agents for nearly all crops, wheat, oats, barley, potatoes, turnips, peas, beans, and grass lands.

### Calcareous Manures.

Under this heading may be classed those mineral compounds in which lime, with its carbonate and sulphate, predominates. They comprise lime, calcareous marls, and gypsum. The mountain limestone found in many districts of England and Scotland is the source of the lime used. Limestone is a carbonate, and lime the oxide of calcium, and for the conversion the limestone is heated to bright redness with fuel in specially contrived kilns, with the result that the carbonic acid is driven off, leaving the lime behind. The following equation represents this action :—

$$CaCO_3 = CaO + CO_2.$$
Limestone = Lime + Carbonic acid.

A pure carbonate yields 56 per cent. of lime, or a little more than half its weight. On long exposure to the atmosphere this action is reversed, the lime absorbs carbonic acid from the air, becoming again a carbonate of lime, thus—

$$CaO + CO_2 = CaCO_3.$$
Lime + Carbonic acid = Carbonate of lime.

A lime, to retain its strength, should be kept well covered when not used. Lime fulfils a double part in agriculture,—

firstly, as a food, it is found in the ashes of nearly all cereal and root crops, as will be seen from the following table, by Dr. Griffiths (*Journal of the Chemical Society*):—

| | |
|---|---|
| Mangel-wurtzel (roots) . . | 13·62 per cent. |
| Meadow hay . . . . | 18·31 „ |
| Beans . . . . . | 7·12 „ |
| Cabbages . . . . . | 15·66 „ |
| Wheat (grain) . . . | 10·66 „ |
| Turnips (roots) . . . . | 13·02 „ |
| „ (leaves) . . . . | 35·62 „ |
| Potato (tubers) . . . . | 3·02 „ |
| „ haulm . . . . | 17·07 „ |

—therefore it will be seen that no crops can grow to perfection without lime; and secondly, its chemical and physical action on the soil is of great value to the farmer. Lime corrects the "sourness" in soils,—that is, neutralises its acidity by rendering innoxious the free organic acids which give a certain harshness to all vegetation. In decomposing decaying vegetable matter, lime plays a very important part, according to Liebig, in destroying the fungi formed by decaying organic matter, and thus preventing the "sickening" of such deep-rooted plants as turnips, clover, peas, beans, etc. Lime also acts chemically upon insoluble forms of mineral matter in the soil, decomposing them, and rendering a portion of their constituents available as a food for the plant.

## Marls.

Marls may be considered as a combination of calcareous and argillaceous clays, one or the other predominating, according to the region in which they are found. In the limestone formations a marl will be practically a carbonate of lime or limestone; on the other hand, a red marl of the Triassic age contains but a small percentage of

carbonate of lime, and as the agricultural value of a marl depends on the carbonate it contains, the red marls, from their deficiency, may be considered of little value to the farmer. According to Dr. Griffiths, the analysis of a sample of chalk-marl gave—

| | |
|---|---|
| Carbonate of lime | 69·23 |
| Phosphate of lime | 0·63 |
| Potash and magnesia | 0·45 |
| Sulphate of lime | Trace |
| Oxides of iron and alumina | 0·36 |
| Soluble silica | 8·29 |
| Sand | 18·55 |
| Moisture | 2·49 |

Marls are valuable additions to land, containing but little lime. Chemically their action is the same as that of lime, but their action is not so rapid.

## Gypsum.

Gypsum, as found in commerce, is a hydrated sulphate of calcium, and, when burnt, forms the well-known plaster of Paris. In a crystalline or fibrous state it exists as alabaster or satin-spar. When gypsum is resolved into its constituents, lime, sulphuric acid, and water are the results, and as these are nutritive substances its value as a food supply to the plant is seen. For grass and meadow lands, potatoes, turnips, and clover, gypsum forms an efficient manure in developing the growth. As regards the latter, Dr. Pincus, in some interesting investigations, shows the increase of the crop, when manured with gypsum, to be—

| | Cwt. of Clover Hay per acre. |
|---|---|
| Without manure | 34·56 |
| With gypsum | 48·96 |

Gypsum also plays a very important part in liberating potash and magnesia in the rock materials of the soil, converting them into a soluble condition for assimilation in the plant. This action is no doubt due to the liberated sulphuric acid acting on the earthy matter, and this acid increases in proportion to the gypsum used. In the ash of air-dried clover hay Dr. Pincus found—

| | Plot unmanured. | Manured with Gypsum. |
|---|---|---|
| Sulphuric acid . | 6·95 per cent. | 7·96 per cent. |

A dressing of 2 cwt. gypsum to an acre is sufficient for this manure.

## Prepared Nitrogenous Manures.

All nitrogenous materials, whether of an inorganic or organic nature, and depending for their value on the nitrogen they contain, will be treated under this heading.

### Ammoniacal Compounds.

Ammonia combines with all the mineral acids, forming a series of compounds soluble in water. They are given with their available nitrogen and values as follows:—

| | Percentage of Nitrogen. | Value per ton. |
|---|---|---|
| Ammonium sulphate $(NH_4)_2SO_4$ . . | 21·21 | £11 |
| Ammonium chloride $(NH_4)Cl$ . . | 26·16 | 37 |
| Ammonium nitrate $(NH_4)_2NO_3$ . . | 42·85 | 32 |
| Ammonium carbonate $(NH_4)_2CO_3$ . | 29·16 | 35 |

It is thus seen that the cheapest source of nitrogen in all the ammoniacal compounds suitable for agricultural purposes is the sulphate. Ammonia (from which the sulphate is made) is derived from many sources. Those, however, of commercial value may be said to be—

(1) The gases from the smelting of iron ore with coke in the blast furnace. They contain nitrogen, hydrogen, carbonic oxide, and carbonic acid, the nitrogen varying from 50 to 52 per cent. of their volume. As the gases issue from the furnace mouth a lowering of the temperature brings into action a chemical union of the larger portion of the nitrogen with the hydrogen and carbonic acid, forming ammonia and ammonium carbonate respectively The gases are drawn through large perpendicular condensers and scrubbers, are condensed and form ammoniacal liquor and tar, the former separating from the latter through a difference in the specific gravity. The ammoniacal liquor on separation is distilled with steam, the vapours passing into sulphuric acid for absorption. On saturation the sulphate is deposited as a grey crystalline powder, which, after draining and exposure for two or three days, is ready for manurial purposes.

(2) As a bye-product in the carbonisation of fuel for illuminating purposes.

The vapours from the gas retorts may be classed as condensable and non-condensable. The non-condensable portion, after purification, is stored in large gasometers for use in the lighting of our streets. The condensable portion contains the larger part of the nitrogen of the coal carbonised, and forms the tar and ammoniacal liquor of the gas works, and from the latter the ammonium sulphate is made, as previously described.

The yield of sulphate is considerable. On an average 1 ton of Lancashire coal yields 10,000 cubic feet of gas, and 20 to 25 gallons of ammoniacal liquor at 5° T., and this is equal to 30 lb. sulphate of ammonia.

(3) In the carbonisation of small coal for the manufacture of coke for smelting purposes by the Simon-Carves, Semet-Solvay, and other ovens, the condensed gases produce a good return of ammonia.

Westphalian coal (Germany) yields on carbonisation for coke about fourteen per cent. of ammoniacal liquor at 4° B., equal to a production of 1 ton ammonium sulphate per 100 tons dry coal coked. An average English coal for coking yields about 22 cwt. per 100 tons dry coal.

(4) Another source of ammonia is the destructive distillation of shale, as carried on by the Scotch mineral oil companies. The yield of ammonium sulphate will range from 16 to 18 cwt. per 100 tons shale treated.

(5) In the carbonisation of bones for the manufacture of animal char, a further supply of ammonia is obtained. This is treated fully under "Animal Charcoal."

Sulphate of ammonia is a chemical combination of the gas ammonia with sulphuric acid.

$$2\ NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

Ammonia + sulphuric acid = ammonium sulphate.

The product commercially has a grey colour, due to tarry matter in a very fine state of division spread through the mass. Two analyses by the author gave the following results:—

| | (1) | (2) |
|---|---|---|
| Moisture . . . . | 3·51 | 5·72 |
| Sulphate of ammonia . | 94·87 | 93·26 |
| Organic matter . . | ·85 | ·54 |
| Mineral matter . . | ·77 | ·48 |
| | 100·00 | 100·00 |

Equal to ammonia ($NH_3$) (1) . . 24·43 per cent.
(2) . . 24·02 „

The production of sulphate of ammonia in this country is about 120,000 tons per annum, this amount being practically all used for agricultural purposes.

The value of sulphate of ammonia naturally depends on

the nitrogen it contains and the rapid manner it diffuses itself through and is thus absorbed by the soil.

Sulphate of ammonia (through its nitrogen) exerts a very important influence in the nutrition of plants, predominating in many plants, including barley, oats, and wheat—the latter, when dry, yielding 17 lb. of nitrogen to the ton of cereal, being equal to the consumption of 80 lb. sulphate of ammonia. Although beneficial for both, it diffuses itself, and thus acts more readily on light, sandy soils than on heavy, clayey lands. On calcareous soils it is considered equally effective, although it has been urged that the action of the lime constituents of the soil on the sulphate of ammonia would result in the formation of a volatile carbonate of ammonia or ammonia, and thus lessen the fertilising power of the sulphate. Hence the advocacy of sodium nitrate in its place. For all root crops, grass lands, and cereals, sulphate of ammonia has been proved by the most practical authorities to be an invaluable manure; and regarding the experiments on wheat crops carried on by the late Sir J. B. Lawes, Liebig gives his approval by saying that, "All the experiments of Lawes in England have shown that for 1 lb. of salts of ammonia in manures, 2 lb. of wheat may be reaped."

### Sodium Nitrate.

Sodium nitrate, commercially termed Chili saltpetre, is a combination of the metal sodium with nitric acid, the latter providing the nitrogen (16·4 per cent.) on which the value of the saltpetre depends.

The commercial product contains 95 to 97 per cent. of pure nitrate, and contains, according to the following analyses by the author—

| | (1) | (2) |
|---|---|---|
| Sodium nitrate . . | 96·39 | 97·60 |
| ,, sulphate . . | ·56 | ·39 |
| ,, chloride . . | ·76 | ·41 |
| Oxide of iron . . | ·12 | Trace |
| Insoluble matter . . | ·82 | ·57 |
| Water . . . . | 1·35 | 1·03 |
| | 100·00 | 100·00 |

From the province of Tarapaca in South America we derive by far the major portion of the nitrate used in this country. The crude deposits, or "caliche" as they are called, are found in beds from four to twelve feet in thickness, and are mined in three qualities, the richest averaging 55 per cent. of nitrate of soda. The "caliche" is a mixture of sodium nitrate with the chloride and sulphate of soda and the sulphates of lime and magnesia, and the nitrate is separated by a careful system of lixiviation. The exportation now reaches the enormous figure of 800,000 tons per annum.

Nitrate of soda and sulphate of ammonia are the two chief sources of nitrogen, being readily soluble, and diffusing with rapidity through the soil. Experiment has, however, shown that on a dry soil the best results are obtained from nitrate.

For many crops nitrate alone, or in conjunction with common salt, forms an excellent manure. In oats, wheat, and barley, the increase of grain with its use is 18 to 19 per cent.

As a top-dressing for turnips, potatoes, peas, and other edible plants, it is unequalled. According to Dr. Slutzer, nitrate of soda does not unduly exhaust the land, and that by it the plant foods are rendered more assimilable for nutrition.

About 1½ to 2 cwt. nitrate of soda per acre, as a top-dressing, is sufficient for most crops.

### Potassium Nitrate.

Potassium nitrate, or the nitre of commerce, is similar in its action to the soda salt. The available nitrogen, however, is much less, being 13·8 per cent. in the pure salt.

Potassium nitrate is rarely used for agricultural purposes, the far cheaper soda salt fulfilling all the reqnirements of a nitrate.

The pure salt has a composition of—

| | |
|---|---|
| Potassium . . . . . | 38·67 |
| Nitrogen . . . . . | 13·86 |
| Oxygen . . . . . | 47·47 |
| | 100·00 |

### Organic Nitrogenous Matters.

Organic nitrogenous matters, as shoddy, ground hoofs and horns, soot, leather waste, dried blood and meat, damaged seed cakes, etc., are also used to a limited extent as nitrogenous manures. Their nitrogen being in an insoluble form, however, the action on the soil is very slow, and consequently their nutritive value is low. For this reason they can never supplant the soluble ammonia or soda salts as a fertiliser.

*Shoddy.*—Shoddy is a refuse product from the textile industries, and contains, when dry, about seven to eight per cent. of nitrogen. It is not prepared by any chemical treatment, but spread on the land in its raw state.

*Hoofs and Horns.*—Hoofs and horns are picked from the raw bones before degreasing, and crushed to a fine powder. In this form they are mixed to a limited extent with superphosphates. They contain 12 to 14 per cent. of nitrogen.

*Soot.*—Soot is unburnt coal, and forms the black carbonaceous mass issuing from the many chimneys of our industrial centres. That the amount floating in the atmos-

phere is large may be gathered from the investigations of Dr. Cohen. He estimates that over the four square miles of Leeds 300 cwt. = 1·2 milligrams per cubic foot, are suspended at any moment, and that 20 tons of soot go into the air daily. That this must have a certain influence on the growth of vegetation may be understood, when it is considered that soot contains 2 to 5 per cent. of nitrogen, and that part of this nitrogen exists as sulphate, which, on dissolving by the rains, is carried to the soil as a fertiliser.

Soot can be used with good effect on vegetables and cereal crops, and also as a top-dressing. In its use 40 to 45 bushels per acre are advisable. Dr. Griffiths gives the following analysis of a sample of soot:—

| | |
|---|---|
| Moisture | 7·39 |
| Organic matter | 43·09 |
| (Containing nitrogen . 0·21 | |
| Equal to ammonia . 0·25) | |
| Sulphate of ammonia | 12·72 |
| Oxides of iron and alumina | 6·51 |
| Carbonate of lime | 10·63 |
| Carbonate of magnesia | 1·84 |
| Alkalies | 2·70 |
| Insoluble silica | 15·12 |
| | 100·00 |

*Leather Waste.*—Leather waste is of little value when applied as such to the soil. Sometimes it is brought into the market in a prepared state. This is done by treating the leather with superheated steam, and drying the mass; by this means the nitrogen becomes in a more soluble condition. Its use is, however, very limited. The percentage of nitrogen averages 5 per cent.

*Dried Meat.*—This is the residual matter in the manufacture of beef extract, dried and powdered. It is not used to any great extent for manurial purposes. When not

adulterated with ground bones, the nitrogen averages about ten per cent.

*Dried Blood.*—Blood may be considered as the most valuable of all the organic nitrogenous manures. Becquerel and Rodier give the analysis of raw or natural blood as follows:—

| | |
|---|---|
| Water | 77·900 |
| Fibrin | ·220 |
| Fatty matters | ·160 |
| Serolin | ·002 |
| Phosphorised fat | ·049 |
| Saponified fat | ·100 |
| Cholestrin | ·009 |
| Albumin | 6·940 |
| Blood corpuscles | 14·000 |
| Extractive matters and salts | ·620 |
| | 100·000 |

When blood is allowed to stand it quickly coagulates, the corpuscles and fibrin separating as a clotted mass from the serum or watery portion. The coagulated mass is separated in a practical way by gravitation or by the centrifugal, and is sold to a limited extent as a manure. The analysis is as follows:—

In 100 parts—

| | |
|---|---|
| Water | 68·80 |
| Solid constituents | 31·20 |
| | 100·00 |

The solid constituents gave—

| | |
|---|---|
| Hæmatin | 1·675 |
| Globulin and membrane of corpuscles | 28·222 |
| Fat | ·231 |
| Extractive matter | ·260 |
| Mineral matter, without iron | ·812 |
| | 31·200 |

The ash or mineral matter gave—

| | |
|---|---|
| Sulphuric acid . . . . | ·81 |
| Phosphoric acid . . . . | 13·96 |
| Chlorine . . . . . | 20·76 |
| Potassium . . . . . | 41·02 |
| Sodium . . . . . | 12·95 |
| Oxygen . . . . . | 8·21 |
| Phosphate of lime . . . . | 1·40 |
| Phosphate of magnesia . . . | ·89 |
| | 100·00 |

As stated, this manure has but a limited sale. It contains a heavy amount of water, and rapidly decomposes.

The concentrated or dried blood in the market is a better manure and easier worked.

In the treatment of blood several methods are in use for producing a dry, powdery manure, amongst which may be mentioned the addition of a mixture of sulphate of iron and alum; the treating of blood with peat and chalk; the precipitation with alkaline phosphates or sulphates; and Delacharlonny's method of producing a solid manure by means of acid ferric sulphate in the place of the neutral sulphate.

Dried blood contains about twelve per cent. of nitrogen, and is an effective manure for all plants, and more especially for cereals and root crops.

### Superphosphates.

From the union of phosphoric acid with calcium are built up three distinct varieties of phosphates—

(1) Mono-calcic phosphate ($CaH_4P_2O_8$).
(2) Bi-calcic phosphate ($Ca_2H_2P_2O_8$).
(3) Tri-calcic phosphate ($Ca_3P_2O_8$).

The mono-calcic phosphate is soluble in water, and forms the "soluble phosphate" of the manure-maker. Under certain conditions, the second is the result of the reaction between the soluble and insoluble phosphates of the super-phosphates of commerce. It is insoluble in water.

The third is the insoluble phosphate of all the mineral and bone products used in the manufacture of super-phosphates.

By acting upon the third or tri-calcic phosphate, we obtain the first or mono-calcic phosphate with two equivalents of calcic sulphate, forming the super-phosphate of commerce. If pure tri-calcic phosphate and sulphuric acid are mixed together according to their combining proportions, we obtain the following reaction :—

$$\underset{(310)}{Ca_3P_2O_8} + \underset{(198)}{2\,H_2So_4} = \underset{(234)}{CaH_4P_2O_8} + \underset{(272)}{2\,CaSo_4}$$

Tri-calcic phosphate + Sulphuric acid = Soluble mono-calcic phosphate + Calcic sulphate

310 parts of phosphate require 198 parts of sulphuric acid to combine and form 234 parts of soluble phosphate (which gives the value to the manure) and 274 parts of sulphate of calcium or gypsum, which possesses little nutritive value; or, to put it in another way, 1 ton pure mineral phosphate requires 12·64 cwt. of sulphuric acid, and yields 1·6 tons (1 ton 12 cwt. 2 qrs. 14 lb.) of superphosphates ($CaH_4P_2O_8 + 2CaSo_4$) containing 53·75 per cent. of mono-calcic or soluble phosphate.

In practice this high percentage is not attainable for the reason that the manufacturer works with a mineral or bone product, varying in the former from 45 to 75 per cent. of pure tri-calcic phosphate, and in the latter, 52 to 60 per cent. In mineral phosphates we find as impurities, carbonate of lime, fluoride of lime, alkaline salts (mainly common salt),

and oxide of iron and alumina. Degelatinised bones contain a considerable proportion of carbonate of lime. All these form sulphates when the mineral or bone is treated with an acid, and remain inseparate from the superphosphate formed, reducing the soluble phosphate down to 25 or 30 per cent.

Again, the consumption of acid is very materially increased by their presence, as is seen by the following table, and thus the cost of working becomes greater :—

| 100 parts of— | | | | | |
|---|---|---|---|---|---|
| Tri-calcic phosphate require | | 63·8 | parts of | sulphuric | acid. |
| Carbonate of lime | ,, | 98·0 | ,, | ,, | ,, |
| Calcium fluoride | ,, | 125·64 | ,, | ,, | ,, |
| Alumina | ,, | 288·23 | ,, | ,, | ,, |
| Ferric oxide | ,, | 183·75 | ,, | ,, | ,, |

The carbonate of lime, when not in excess, in addition to forming gypsum, which acts as a dryer to the superphosphate, also gives it a certain sponginess and lightness. Calcium fluoride has no value, and the hydro-fluoric gas produced from its decomposition is a nuisance to the mixer. Alumina and ferric oxide are the reverse of beneficial to the superphosphate, acting on the "soluble," and reconverting it to the "insoluble" phosphate.

The soluble and insoluble phosphates from bone or char are worth more than the same percentages in a mineral superphosphate, due to a quicker assimilation in the soil, and with a higher fertilising power. Manufacturers generally sell on a basis of 32 to 34 per cent. of soluble phosphates (calculated as tribasic), and 2 to 4 per cent. insoluble.

The following are three samples of superphosphates analysed by the author, and made from—(1) spent char; (2) equal parts of degelatinised bones and mineral phosphates; and (3) mineral phosphates solely :—

| | Spent char. | Equal parts of degelatinised bones and mineral phosphates. | Mineral phosphates. |
|---|---|---|---|
| Total moisture . . | 12·17 | 16·39 | 20·26 |
| Organic matter . . | 11·39 | 6·45 | ... |
| Mono-calcic phosphate [1] | 24·90 | 24·39 | 25·58 |
| Tri-calcic phosphate . | 2·51 | 4·14 | 3·07 |
| Sulphate of lime . | 43·33 | 40·24 | 39·68 |
| Ferric and aluminic sulphates . . | ·84 | 2·23 | 5·01 |
| Magnesium sulphate . | ... | ·64 | 1·92 |
| Alkaline sulphates . | 3·07 | 1·31 | ... |
| Insoluble matter, silica | 1·79 | 4·21 | 4·48 |
| | 100·00 | 100·00 | 100·00 |
| [1] Equivalent to tribasic phosphate of lime . . | 33·00 | 32·05 | 33·89 |

Degelatinised bones and mineral phosphates require to ground to a meal before elevation to the mixing trough. Bone char or spent char, being in a fine granular condition, requires no preparatory grinding. With mineral phosphates it is essential that a degree of fineness be attained which will enable them to pass through a 50-mesh sieve without any "tailings." The grinding is carried out by a triple set of millstones. In Figures 11, 12, and 13, are shown the longitudinal section and upper and ground floor plans respectively of a modern manure-shed measuring 40 feet long by 23 feet high from the floor to the ridge of the roof.

*A* represents the triple set of millstones fitted up in a lean-to building adjoining the main building, and called the "grinding-house," each set being worked by two bevelled cog-wheels underneath, and driven from the shaft *N*. The stones are made of the hardest French "burrs" on edge, and have a diameter of 4 feet 6 inches. They can be regulated to grind to any degree of fineness required. From the millstones the ground materials pass by a "shute" to the "boot" of the elevator *B*, which is vertically arranged and

closed the whole length by a wooden cover. It is driven by

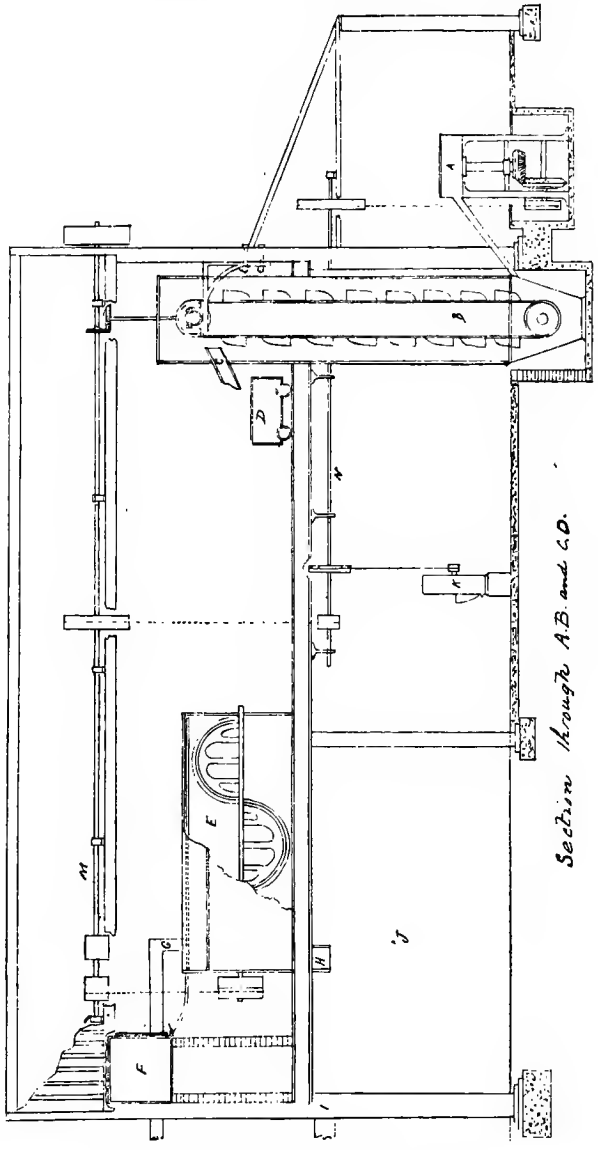



Fig. 11.

two cog-wheels from the shaft *M*. The elevator lifts the

ground phosphate to the upper floor (Fig. 12), thence falling through the shute *C* to the bogie *D*, by which it is carried to the mixing-trough *E*. The trough is built of stout 2-inch timber, lead-lined, and has a measurement of 12 feet by 5 feet by 5 feet, is bevelled at the top, and fed through a sliding-door fixed on the bevel, from the bogie. Through the centre of the trough runs a shaft carrying the spiral mixer, which is driven from the pulley on the shaft *M*. *F* is a lead-lined tank 3 feet square and supported on brick columns, for holding the sulphuric acid used, the acid being conveyed to the trough by a lead pipe, fitted with necessary stopcock and running the length of the mixer, that portion of the pipe within the trough being perforated to allow the acid to spray over the mass.

The tank holds about 168 gallons, and on the outside a scale divided into inches is fixed, each division corresponding to a known weight of acid, and thus at a glance the workman can see the number of inches used.

During the mixing in the trough, hydrofluoric, carbonic, and other deleterious acid gases are evolved from the chemical actions taking place. They are drawn through the outlet pipe *G*, by an exhaust fan, into condensers and scrubbers, whereby the noxious vapours are removed by condensation. In many country works manufacturers do not trouble themselves about the penalties attached to an offence under the Noxious Vapours Act; they do not care to lay out expense in suitable condensing arrangements, consequently the gases, untreated in any form, pass into the works chimney, and vegetation suffers for the neglect.

When the mixing is completed, the sliding-door at *H* is opened, and by the action of the spiral the hot and soft mass is forced through into a large chamber or "den" *J*, as it is termed, placed directly underneath. The "den" is a brick-lined building running the height of the ground floor, and

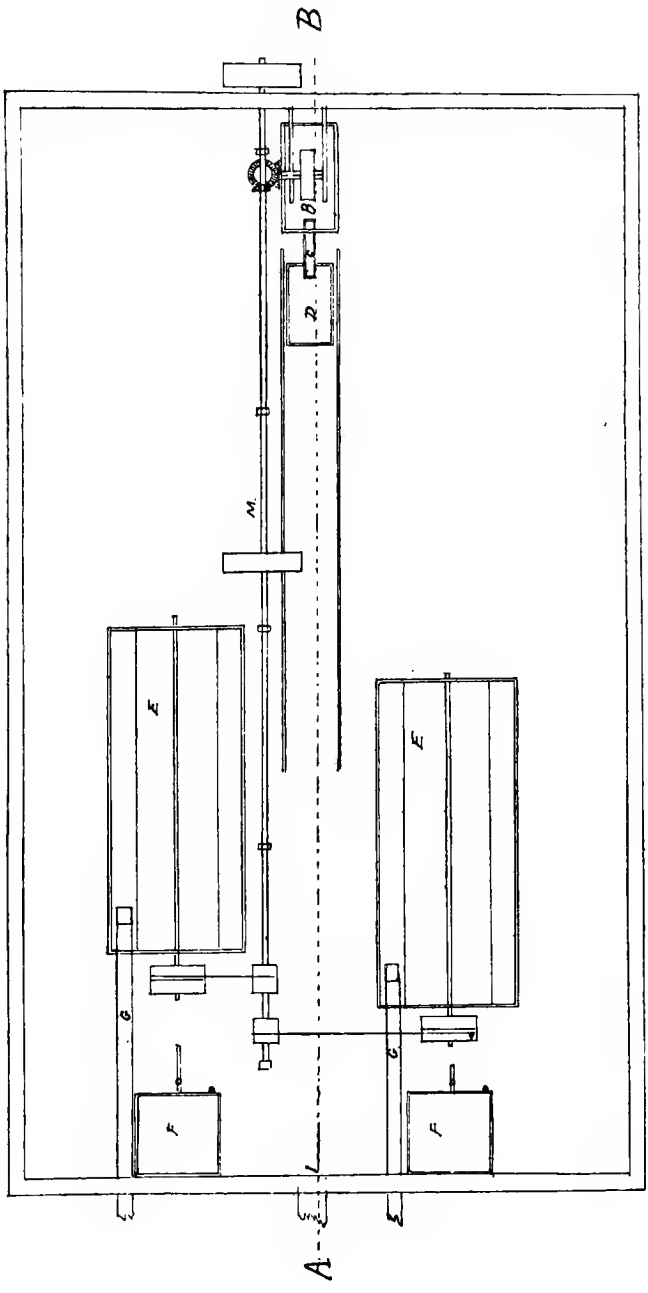


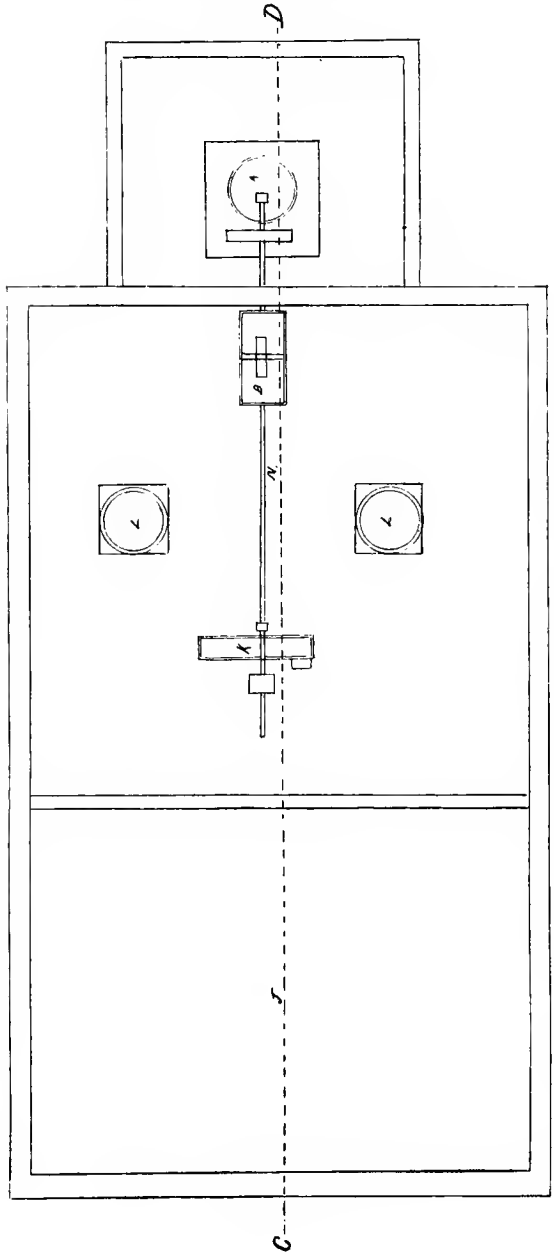

FIG 12.

has a length of 16 feet, width 22 feet, and height 9 feet. At the corner *I* is placed an outlet pipe, in connection with *G*, by which the noxious gases are removed to the condensers.

The front of the den is provided with a large door, through which the superphosphate, after drying and cooling, is conveyed to the disintegrator *K*, driven from the shaft *N*. Here the hard and lumpy material is crushed to a coarse powder, and made ready for mixing, with suitable proportions of kainite, ammoniacal salts, dried blood, or other nitrogenous matters, to form the "artificials" for cereal, root, grass, or other crops. This is done by spreading out a little the coarse superphosphate, adding the necessary ingredients in the proportions required, turning the heap over once or twice, and finally passing through the mixers *LL*, as shown in Fig. 13. The manure is now ready for bagging.

In gauging the amount of acid required the manufacturer must consider its strength, and also the nature of the phosphate he is dealing with. A phosphate containing a low excess of lime over the quantity required to form tri-calcium phosphate, and which goes to form carbonate, and probably fluoride of calcium, and with a low proportion of iron and alumina, consumes less acid and yields a richer superphosphate; on the other hand, if the excess of lime be considerable, with higher proportions of alumina and iron present, the consumption of acid will be greater and a weaker superphosphate produced, for, from the table previously given, it will be noticed that while 100 parts of tri-calcium phosphate requires for conversion 63 parts of acid, carbonate of lime consumes 98 parts, calcium fluoride 125 parts, or nearly double, and iron and alumina 183 and 288 parts respectively. Consequently the purer the phosphate the more economical is it worked, and the richer the superphosphate produced.

For mixing purposes the most suitable acid is found to be the quality described as "chamber acid," having a specific




Plan of Ground Floor.
FIG. 13.

gravity of 1·57, equal to a Twaddell strength of 114°. Acid of this strength contains 85 per cent. of anhydrous sulphuric acid and 15 per cent. of water. Of the latter, a portion is given off as steam during the chemical action in the trough, which generates a high temperature; the remainder unites with the sulphate of lime formed to dry the superphosphate.

A charge of 8 to 9 cwt. of ground phosphate is allowed each trough, the conversion on the addition of the acid taking about eight minutes. Each trough, then, of the dimensions given will produce from 6 to 7 tons superphosphates per hour, or, in a working day of ten hours, 60 to 70 tons, which is ready for removal every alternate day from the den below.

The following represent some "mixings" for superphosphate:—

*High-Class Superphosphates.*

| | Cwt. | Qrs. | Lb. |
|---|---|---|---|
| Acid (spec. grav., 1·57) . . | 4 | 2 | 16 |
| Spent char . . . . | 3 | 0 | 0 |
| New char siftings . . . | 3 | 0 | 0 |

*Special Black Superphosphates.*

| | Cwt. | Qrs. | Lb. |
|---|---|---|---|
| Char siftings . . . . | 6 | 0 | 0 |
| Acid (spec. grav., 1·57) . . | 4 | 3 | 8 |

*Bone Superphosphates.*

| | Cwt. | Qrs. | Lb. |
|---|---|---|---|
| Acid (spec. grav., 1·57) . . | 6 | 0 | 0 |
| Degelatinised bones, and spent char | 7 | 2 | 0 |

*Mineral Superphosphates.*

| | Cwt. | Qrs. | Lb. |
|---|---|---|---|
| Acid (spec. grav., 1·57) . . | 7 | 1 | 12 |
| Mineral phosphates . . . | 8 | 0 | 0 |

Taking the average of mineral phosphates, the consumption of acid is about 92 per cent. of the weight of phosphate taken.

Superphosphates supply to the soil lime, sulphuric and

phosphoric acids. The phosphoric acid, with its combining proportion of lime as mono-calcic phosphate, is quickly absorbed by the rootlets of the plant. The remainder of the lime, in combination with sulphuric acid as sulphate of lime, gives up but slowly, by decomposition in the soil, its nutritive constituents.

Although forming a valuable manure for all grain and root crops, superphosphates are not often used alone, but in conjunction with certain proportions of potash and ammoniacal salts, forming the mixed or special manures compounded to suit any particular crop.

## Special or Mixed Manures.

Although the ashes of plants consist of several mineral ingredients, yet we may safely conclude that they depend for their existence primarily on the potash, phosphoric acid, and nitrogen abstracted from the soil, and these will vary in their absorptive amounts according to the class of plant. For instance, nitrogen is the dominant nutritive required by wheat, oats, rye, grass, and other plants; with beans, clover, potatoes, etc., potash is needed; while for maize, turnips, and other crops, phosphates are the main food absorbed, along with potash and ammonia. With this knowledge, the maker is in a position to build up a manure suitable for any desired crop.

All special manures are sold to the farmer on a guarantee, in conformity with the strength of manure manufactured, and, with a knowledge of the unit values of potash, nitrogen, and phosphoric acid, he can readily estimate their value and judge whether he is overcharged. With manure manufacturers of standing, adulteration is not carried on, and their guarantee can be depended on as an average of the bulk to be supplied.

The following are the leading "artificials" made, with their guarantees of strength :—

(1) *Special early Potato Manure.*

| | |
|---|---|
| Sulphate of potash . . | 3 to 5 per cent. |
| Soluble phosphates . . | 20 to 22 ,, |
| Insoluble phosphates . . | 2 to 4 ,, |
| Ammonia . . . . | 10 to 11 ,, |

(2) *Special Potato Manure.*

| | |
|---|---|
| Sulphate of potash . . | 8 to 10 per cent. |
| Soluble phosphates . . | 28 to 30 ,, |
| Insoluble phosphates . . | 1 to 2 ,, |
| Ammonia . . . . | $3\frac{1}{4}$ to $3\frac{3}{4}$ ,, |

The mixings per ton being—

| | |
|---|---|
| Superphosphates . . . . | $12\frac{1}{2}$ cwt. |
| Kainite . . . . . | $5\frac{1}{2}$ ,, |
| Sulphate of ammonia . . . | 2 ,, |

The manure being applied 5 to 6 cwt. per acre.

*Special Manure for Turnips, Mangels, etc.*

| | |
|---|---|
| Sulphate of potash . . | 3 to 4 per cent. |
| Soluble phosphates . . | 26 to 28 ,, |
| Insoluble phosphates . . | 2 to 4 ,, |
| Ammonia . . . . | 3 to 4 ,, |

The mixings per ton being—

| | |
|---|---|
| Superphosphates . . . . | 15 cwt. |
| Kainite . . . . . | 3 ,, |
| Sulphate of ammonia . . . | 2 ,, |

The quantities used are 5 cwt. per acre.

A good manure for mangels, turnips, etc., should contain 30 to 32 per cent. of total phosphates, with 26 to 28 per per cent. as soluble, and moderate proportions of potash and ammonia. The manure is spread broadcast after seed-time, and then covered in.

*Dissolved Bones.*—The following is a good strength for this manure:—

| | |
|---|---|
| Soluble phosphates . . | 21 to 23 per cent. |
| Insoluble phosphates . . | 10 to 12 „ |
| Ammonia . . . . | 3 to 3¼ „ |

This manure is generally made from degreased bones (not boiled), by treating them, in a crushed state, with sulphuric acid. The mass is then mixed with a small proportion of bone dust to dry up the manure, allowed to harden, one to two days, then passed through the disintegrator to break up any lumps, and bagged in the usual way. The bones not being degelatinised, furnish the nitrogen without any addition of ammoniacal salts.

Dissolved bones made from degelatinised bones (bones with the gelatine boiled out) contain more phosphate, but are much poorer in nitrogen, not exceeding 1 per cent. in a well degelatinised bone; if made from raw bones, or bones that have been treated by the benzene process to remove the fat only, then the nitrogen in the bone is retained. This difference in nitrogen in a manure from raw or degreased bones, or from degelatinised or steamed bones, makes a difference in value. Dissolved bones should be bought on the percentages of soluble and insoluble phosphates and ammonia present.

Dissolved bones form a useful all-round manure, being of advantage to nearly all crops. It is best used in early spring, in quantities of about 5 cwt. to an acre of root or grass crops.

*Dissolved Bone Compound.*

| | |
|---|---|
| Soluble phosphates . . | 20 to 21 per cent. |
| Insoluble phosphates . . | 6 to 7 „ |
| Ammonia . . . . | 2 to 2½ „ |

This manure is all bone, and is generally made from

degelatinised bones (bones with the gelatine boiled out) and sulphuric acid; the deficiency in nitrogen is made up by intimately mixing in the required amount of nitrogen in the form of sulphate of ammonia. (132 parts of the salt contains 28 parts of nitrogen.)

The manure is not so strong in phosphates and ammonia as that made from raw or degreased bones, consequently it is cheaper. It has been found of special importance "on cold, clayey, and also still calcareous or damp soils." For promoting the early maturity of turnips, mangels, and other root crops, this manure is very efficacious and economical. The proportions are about 4 cwt. to an acre, and applied at seed-time.

*Dissolved Peruvian Guano.*—In this form guanos are more suitable and economical to the farmer, being quicker in manurial action than raw guanos, and with no loss of valuable ammonia.

A good strength dissolved guano contains the following:—

| | | |
|---|---|---|
| Total phosphates . . | 23 | per cent. |
| Soluble phosphates . . | 21½ | ,, |
| Insoluble phosphates . . | 1½ | ,, |
| Ammonia . . . . | 9 | ,, |

The guarantee is given on the phosphates and ammonia, not on potash or alkaline salts, unless specially required.

This dissolved manure is prepared by treating Peruvian guano with 80 to 82 per cent. of its weight of sulphuric acid in the manure trough, cooling in the "den," and passing through the disintegrator to reduce to a granular condition. The chemical action of the acid fixes the volatile ammonia as sulphate, also the tri-calcic phosphate is converted to the soluble or mono-calcic phosphate, and the manure is left in a dry and granular condition of good strength, and suitable for the drill.

*Enriched Peruvian Guano.*—This manure is sold on the following basis :—

| | |
|---|---|
| Guano phosphates . . | 41 to 43 per cent. |
| Ammonia . . . . | 10 ,, |
| Sulphate of potash . . | 1 to 1½ ,, |

Enriched Peruvian guano is Peruvian guano of medium quality, fortified with sulphate of ammonia, to form a high strength Peruvian guano.

The manure can be applied to all soils not of a calcareous or chalky nature.

*Special Manure for Garden Stuffs, Carrots, Cabbages, Beet-roots, etc.*—The following mixing forms an excellent manure for garden stuffs :—

| | Per ton of manure. |
|---|---|
| Superphosphates . . . | 13 cwt. |
| Sulphate of ammonia . . . | 4½ ,, |
| Kainite . . . . . | 2½ ,, |

—the whole intimately mixed together and applied 6 to 6½ cwt. per acre.

*Special Manures for Grass Lands.*—The following quantities per ton form a nourishing manure when sown on the land. It is recognised that nitrogenous manures increase the quality, while phosphatic manures, and those containing potash, improve the quality of the herbage.

| | |
|---|---|
| Superphosphates . . . . | 11 cwt. |
| Kainite . . . . . | 5 ,, |
| Sulphate of ammonia . . . | 4 ,, |

These ingredients are intimately mixed together, and applied 11 to 12 cwt. per acre.

*Special Tobacco Manures.*—Considerable quantities of manures are now made and sent abroad for the cultivation of tobacco crops. The essential ingredients for the growth

of the plant are phosphates, nitrogen, and potash, and these are compounded on the following basis :—

| | |
|---|---|
| Soluble phosphates . . | 18½ to 19½ per cent. |
| Insoluble phosphates . . | 16 to 17 „ |
| Sulphate of potash . . . | 10 „ |
| Ammonia . . . . . | 5 to 6 „ |

The whole of the phosphates are derived from Peruvian guano, along with part of the ammonia and potash; the remainder is added by an admixture with sulphates of potash and ammonia in the required proportions. Below is an analysis of special tobacco guano, as used by the British Deli Co., Belewan :—

| | |
|---|---|
| Ammonia salts [1] . . . . . | 10·38 |
| Organic matter [2] . . . . . | 12·34 |
| Mono-calcic phosphate [3] . . . | 14·25 |
| Insoluble guano phosphate . . | 16·81 |
| Alkaline salts [4] . . . . . | 10·94 |
| Hydrated calcium sulphate, magnesia, salts, etc. . . . . | 25·89 |
| Moisture . . . . . | 8·21 |
| Insoluble silicious matter . . | 1·18 |
| | 100·00 |

| | |
|---|---|
| [1] Containing active soluble ammonia . | 2·67 |
| [2] Containing organic assimilable ammonia | 2·64 |
| Total ammonia . . . | 5·31 |
| [3] Equivalent to tribasic phosphate of lime | 19·00 |
| Insoluble guano phosphates . . . | 16·81 |
| [4] Containing sulphate of potash . . | 10·54 |

*Special Sugar-Cane Manure.*—This manure is generally prepared from spent char, and with the following strength :—

| | |
|---|---|
| Soluble phosphates . . . | 19 to 20 per cent. |
| Insoluble phosphates . . | 3½ to 4½ „ |
| Potassium sulphate . . . | 9 „ |
| Ammonia . . . . . | 10 to 11 „ |

Sulphate of ammonia has been used for enriching the juice of the cane, but this fertiliser can only act with advantage when the soil contains the necessary amounts of lime and magnesia. In using a manure containing lime in a combined state, any deficiency of this ingredient in the soil is restored by the decomposition of the calcium phosphate and calcium sulphate, forming part of the manure.

It has been urged that the farmer should compound his own manures instead of buying. The suggestion is not an impracticable one, for, with a knowledge of the nutritive requirements of each crop, and the source from which these nutritives can be obtained, no great skill is required from the farmer in building up a manure of any desired strength, and at a considerably less cost than what he would purchase it for.

A manure is not a chemical combination, but a mechanical mixture of certain ingredients required to suit a particular crop, and the weighing and mixing of these ingredients can be done as well on the farm as at the manure works. The mixing must be carried on in a dry shed, and then bagged for use at any season.

Suppose the farmer wishes to make a manure of the following strength :—

| | |
|---|---|
| Soluble and insoluble phosphates . . | 26 per cent. |
| Sulphate of potash . . . . . | 4 „ |
| Ammonia . . . . . | 10 „ |

suitable for any root crop. The phosphates he would buy as superphosphates, the sulphate of potash as kainite, and the ammonia as sulphate of ammonia from the nearest gasworks, converting their ammoniacal liquors into sulphate.

The phosphates at 26 per cent. would equal 100 parts superphosphates necessary.

The kainite supplying the sulphate of potash contains

only 23 per cent. of that ingredient: then the amount of kainite necessary to supply the 4 per cent. potassium sulphate will correspond to 17½ parts.

The 10 per cent. ammonia is derived from the sulphate of ammonia, 132 parts of which furnish 34 parts of ammonia: then the 10 per cent. requires 38¾ parts of that salt.

Assuming, then, that the parts represent hundredweights, we have the mixing and price as follows:—

| | | | | | |
|---|---|---|---|---|---|
| Cwt. | 100 | superphosphates at £2, 10s. per ton d/d . | £12 | 10 | 0 |
| ,, | 17½ | kainite at £3 per ton d/d . . . . | 2 | 12 | 6 |
| ,, | 38¾ | sulphate of ammonia at £11 per ton d/d . | 21 | 6 | 3 |
| ,, | 156¼ | cwt. = 7 tons 16 cwt. 1 qr., cost . . | £36 | 8 | 9 |

Equal to 4s. 8d. per cwt.

The same strength of manure would be paid for at the rate of £7 per ton. Adding the cost of labour, bags, etc., to the above, the farmer by making this particular manure would effect a saving of £2 per ton.

## Valuation of Manures.

Chemical analysis defines only the composition of a manure. In determining the commercial value, we have to inquire concerning the origin of its constituents—that is, we must find whether the phosphates are from bone or from a mineral source, and if the nitrogen exists as a soluble ammonia salt or is derived from nitrogenous matter. These are necessary inquiries, for bone phosphates have a higher agricultural value than mineral phosphates of equal strength, and the nitrogen of sulphate of ammonia is worth considerably more than the same element, derived from treated leather waste or dried blood. Superphosphates are bought on the amount of soluble phosphate they contain. By this is understood not the actual amount of mono-calcic phosphate which

is the soluble part of the manure, but its equivalent as tribasic phosphate of lime made soluble by acid treatment.

All phosphates, ammonias, and potashes, are now bought at a fixed price per unit. This price naturally varies according to its manufactured or raw state. For instance, a mineral phosphate may be bought at 8d. per unit—that is, 8d. for every percentage of tribasic phosphate present; when treated with acid and rendered soluble, the same unit of tribasic phosphate has a value of 1s. 6d. or 1s. 8d., according to the price ruling. Then, again, the value of the unit of ammonia from sulphate of ammonia may be 15s., and the unit from nitrogenous matter worth only 8s.

In calculating the money value of a manure we assume that the only valuable products in it are phosphates, ammonia, and potash; if, then, we multiply each ingredient by its market price per ton, and add up the values so obtained, we get the total value for 100 tons, which divided by 100 gives the value per ton.

Supposing we have a manure containing in 100 tons—

| | | |
|---|---|---|
| 26 | per cent. | soluble phosphate, |
| 4 | ,, | insoluble phosphate, |
| 10 | ,, | sulphate of potash, |
| $3\frac{1}{2}$ | ,, | ammonia, |

then the value is determined as follows:—

| | | | | | |
|---|---|---|---|---|---|
| 30 | per cent. | phosphates, 30 × £2, 10s., value of superphosphates, per ton . . | £75 | 0 | 0 |
| $3\frac{1}{2}$ | ,, | ammonia = 13·4, say $13\frac{1}{2}$, tons of sulphate of ammonia at £11 per ton . . . . . | 148 | 10 | 0 |
| 10 | ,, | sulphate of potash = $43\frac{1}{2}$ tons kainite at £3 per ton . . | 130 | 10 | 0 |
| | | 100 | 354 | 0 | 0 |
| | | Value per ton . | £3 | 10 | $9\frac{3}{4}$ |

# PART III.

## CHAPTER IX.

### Analysis of Raw and Finished Products.

This chapter is devoted to a description of the methods adopted in making the many analyses required to be conducted in the laboratory of a bone works. They are given as complete as possible, so as to be a guide to the chemist undertaking this important work, the accuracy of which is a matter of great importance to the manufacturer in successfully carrying on the industry. We will commence with the raw material entering the works.

### (1) Common Raw Bones.

Although not bought on any guarantee, the chemist will find it necessary to make a frequent examination of them. The analysis is confined to the determination of the moisture, fat, and nitrogen, the results of the latter giving an approximate idea of the ultimate yield of glue. For this purpose a carefully drawn average of the day's intake is made, comprising ribs, jaws, shoulder-blades, heads, etc. They are coarsely broken, and then passed through a small mill, which reduces the whole to a fit state for analysis, thence intimately mixed together, and an 8 oz. stoppered bottle filled, from which is rapidly weighed out, to prevent any loss of moisture, the amounts required for each determination.

(*a*) *Moisture.*—5 grams are weighed in a porcelain crucible and heated in the air oven for fourteen hours at a temperature of 100° to 105° C., cooled in the desiccator, and

reweighed. The difference in weight represents the moisture, and the percentage is calculated as follows:—

Example—

| | | |
|---|---|---|
| Weight of crucible + bones before heating | . | 18·164 grams. |
| „ „ after heating | . | 17·103 „ |
| Moisture lost | . | 1·061 „ |

On the 5 grams of sample taken the percentage is—

$$\frac{1{\cdot}061 \times 100}{5} = 21{\cdot}22$$

(*b*) *Fat.*—The fat is determined in a Soxhlet's fat extraction apparatus, as seen in Fig. 14. The apparatus comprises a small flask *A*, extractor *B*, condenser *C*, tube *D*, with an opening at the bottom, which is covered with a layer of fine asbestos or glass wool, to prevent any bone particles passing through. The tube is first weighed, then filled three parts full of the sample, and reweighed. The difference is the quantity of the sample taken. It is then inserted in the extractor. The small flask, which must be thoroughly dry, is now tared, and the weight noted. The ether (solvent used) is poured in at the top of the condenser until the flask is about half full, and heat with a Bunsen flame applied to the vessel of water *E*, in which the flask is placed. As the water gradually warms, distillation commences, the ether vapours passing up through one of the limbs of the extractor into the condenser, and, on condensation, trickle down on to the bones within the tube, dissolving out the fatty matter. When the syphon overflow is reached, the

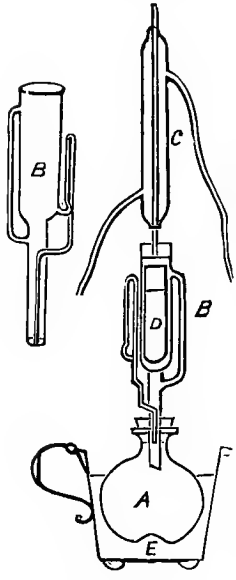


FIG. 14.

ether, with the fat it has dissolved, is syphoned off into the flask below, the ether being again driven off, leaving the fat behind. This is repeated about seven times, when the bones may be safely considered free of any fatty matter. The flask is now disconnected, with its mixture of ether, fat, and water, wiped with a dry cloth, and placed in the air oven for fourteen hours, at a temperature of 100° to 105° C., then cooled, and reweighed. The increase of weight is the fat extracted, from which the percentage is calculated.

Example—

| | | |
|---|---|---|
| Tube + sample . . . | 16·139 | grams. |
| Tare of tube . . . | 9·432 | ,, |
| Sample taken . | 6·757 | ,, |
| Weight of flask + fat . . | 32·243 | ,, |
| Tare of flask . . . | 31·399 | ,, |
| Fat extracted . . | ·844 | ,, |

Then $\frac{\cdot 844 \times 100}{6 \cdot 757} = 12 \cdot 49$ per cent. of fat in the sample.

A check on the percentages of fat and moisture so obtained, can be made by drying the tube containing the degreased bones for fourteen hours at 100° to 105° C. and reweighing; the loss of weight represents the combined fat and moisture, from which the percentage can be readily calculated, and should equal the sum of the two results above found.

(*c*) *Nitrogen.*—The nitrogen is determined by Keldjahl's process. By this method the organic matter is oxidised, the containing nitrogen being converted into ammonia, and is fixed as sulphate of ammonia by the sulphuric acid present. For analysis, 4 grams of the sample are weighed out in a Jena flask, and 15 c.c. of strong sulphuric acid added, along with 8 grams fused bisulphate of potash. The whole is gradually heated on a sandbath at first, until the frothing

is over, and then strongly, till the black carbonaceous mass gives place to a clear, pale yellow liquid. This will occupy about three hours. Remove the flask, cool, and then cautiously fill to the neck with cold water, shaking well after each addition. In Fig. 15 is seen a sketch of the apparatus required to distil over the ammonia formed in Keldjahl's process. A large flask *A* is connected with a receiver *B*

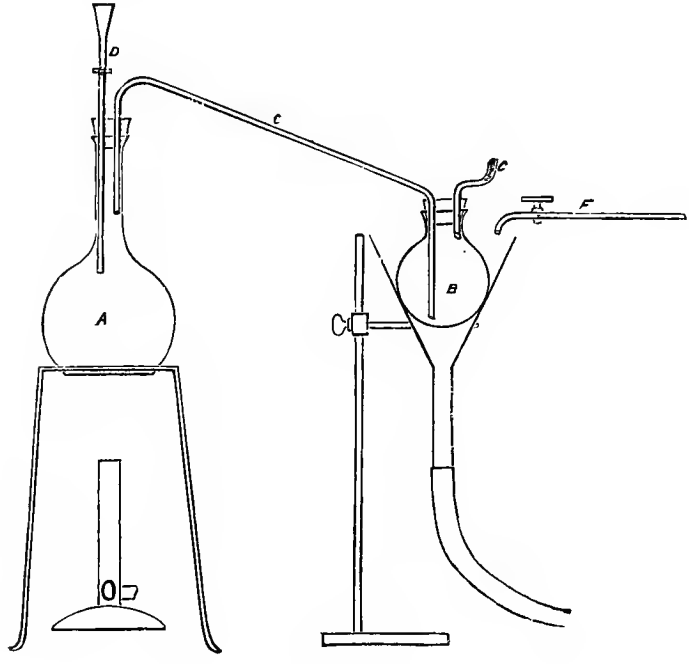



Fig. 15.

by the tube *C*, the lower end dipping under a layer of standard sulphuric acid, *D* is a funnel, with stopcock, for conveying a solution of caustic soda to the flask, *F* a water jet, and *G* the safety funnel, filled with fragments of broken glass. The standard solutions required are sulphuric acid and carbonate of soda, and are of decinormal strength—1 c.c. acid = 1 c.c. alkali. They are prepared in the usual

way. Through the safety funnel of the receiver is run 30 c.c. of the standard acid, the different parts of the apparatus connected and made tight, and an excess of caustic soda solution allowed to flow into the flask. Heat is now applied cautiously, care being taken that no portion of the caustic soda is mechanically carried over. On boiling for an hour, the whole of the ammonia is driven over to the receiver, and there absorbed by the sulphuric acid. The receiver is now disconnected, the safety funnel washed with water, and the washings added, and the whole contents titrated with standard soda solution, according to the well-known volumetric method.

Example—

| | |
|---|---|
| Weight of sample taken . . . . | 4 grams. |
| Decinormal acid used . . . . . | 30 c.c. |
| Retitration with decinormal carbonate of soda . | 17 c.c. |
| Leaving . . . . | 13 c.c. |

Then $13 \times \cdot 014 = \cdot 182$, the amount of nitrogen contained in the 4 grams of the sample, the percentage being $\frac{\cdot 182 \times 100}{4} = 4 \cdot 55$.

For practical purposes, 1 part of nitrogen represents 5·4 parts of glue, then $5 \cdot 4 \times 4 \cdot 55 = 24 \cdot 57$, the percentage of glue corresponding to the above amount of nitrogen.

The manufacturer, naturally, calculates his yield of glue on the bones as "paid" over a weighing machine, and not on a dry sample.

### (2) Degreased Bones.

These are examined daily for any fat left unextracted by the naphtha treatment. This is done in the Soxhlet apparatus, as described at (1) (*b*). The unrecovered fat should not exceed ·5 per cent.

### (3) Crude or Unclarified Fat.

This is tested for any excess of naphtha left in the fat after leaving the mont-jus. The method is described under 'Refined Fat.'

### (4) Refined Fat.

On the analysis of the refined fat depends its value to the consumer. For this purpose it is necessary to estimate the moisture, organic matter other than fat, ash or mineral matter, and fatty acids (Titre). The analysis may be extended to the determination of the saponification equivalent,

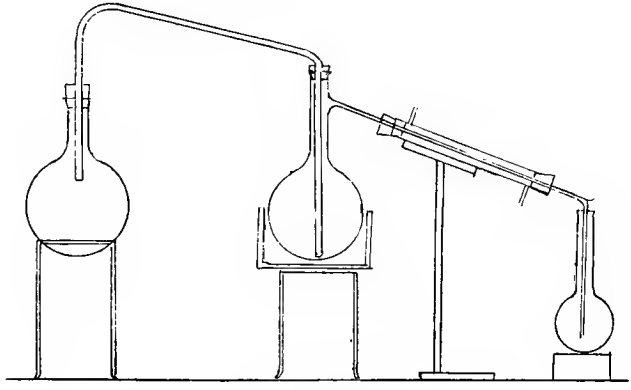


Fig. 16.

and iodine absorption of the fat, but for practical purposes the above are sufficient for the maker.

(*a*) *Moisture.*—This is determined as at (1) (*a*) under the heading of "Raw Bones." It may here be stated that any naphtha the fat contains will be that portion having a high boiling-point, consequently no portion is lost at the temperature of the air oven 100° to 105° C., and thus alter, however slightly, the moisture determination.

(*b*) *Naphtha.*—In estimating the naphtha, 100 grams are

taken and placed in a flask with side tube from neck, fitted to a small Liebig's condenser; to the other end is fixed, with rubber tubing, a bent glass tube, passing into a receiver with a long neck, graduated into $\frac{1}{10}$ c.c., and which is half filled with water. The flask is closed with a cork containing two openings, one for the insertion of a thermometer, and the other for a glass tube dipping down into the fat, the tube being connected with a flask for generating a current of steam. A clip closes the connection between the two flasks; the flask containing the fat is partly embedded in sand on a sand bath, and is heated with a Bunsen burner underneath. (See Fig 16.) The heat is raised to about 165° C., and the clip then opened, and a current of steam blown through the liquid fat for half an hour; this dispels the last trace of naphtha. The vapours are condensed in their passage through the condenser to the receiver, and in the latter will be found any naphtha present, floating as a thin film on the surface of the water. The receiver is now removed and filled with tepid water to about half-way up the graduated neck, then cooled to the normal temperature, and the naphtha read off on the scale.

Example—

Suppose the reading was ·2 c.c.

Then ·2×·730 (specific gravity) = ·146 grams naphtha, and on the 100 grams of the sample taken would be ·146 per cent.

(*c*) *Ash or Mineral Matter.*—About 2 grams of the sample are slowly incinerated in a porcelain crucible, which must be of constant weight, great care being taken that no loss is made by spurting. On reducing the fat to a black carbonaceous mass, the crucible is removed to a muffle, and heated at a red heat for twelve hours; this burns off the whole of the carbon, leaving as a residue the mineral matter. On cooling and weighing, the calculation is made as follows:—

Example—

| | | |
|---|---|---|
| Weight of crucible + ash . . . | 12·641 | grams. |
| Weight of crucible . . . . | 12·638 | ,, |
| Ash | ·003 | ,, |

Then on the 2 grams taken, the percentage is—

$$\frac{\cdot 003 \times 100}{2} = \cdot 150$$

(*d*) *Organic Matter other than Fat.*—This comprises any gelatinous matter abstracted from the bones by careless working, dirt of an organic nature, etc. Take 3 grams of the sample, place in a small beaker, and add carbon disulphide, stir well for a few minutes, and then pass on to a tared filter-paper, wash with portions of carbon disulphide until the filtrate shows no trace of fat, which is known when a drop or two of the filtrate warmed on a watch glass leaves no residue. The filter paper is now dried in the oven, at 100° C. for three or four hours, cooled under dessicator, and reweighed. The difference represents the organic and mineral matter insoluble in the solvent.

Example—

| | | |
|---|---|---|
| Filter paper + residue . . . | ·660 | grams. |
| Tare of filter paper . . . | ·652 | ,, |
| Residue | ·008 | ,, |

Then $\frac{\cdot 008 \times 100}{3} = \cdot 266$ per cent. of mineral and organic matter in the sample.

On deducting the mineral matter (ash) previously found (·266 – ·150), we obtain ·116 as the percentage of organic matter, other than fat, in the sample taken.

(*e*) *Fatty Acids* (*Titre*).—In determining the fatty acids, it is unnecessary to effect an actual separation, the titration

being done direct by a standard solution of caustic soda. The solution is made decinormal by dissolving 4 grams of the caustic soda in water, and making to a litre. This is standardised by a pure alcoholic solution of stearic acid, the strength so being that 1 c.c. should exactly neutralise ·0284 grams stearic acid. The methylated spirit used must be entirely free from any trace of free acid. Five grams of the sample are weighed into a flask, then add 70 c.c. of methylated spirit, shake well, and bring to the boil by immersing the flask in boiling water. When the fatty acids are dissolved, a few drops of an alcoholic solution of phenol-phthalein are added, and the decinormal solution of caustic soda run in gradually from a burette until the characteristic pink tinge is obtained, indicating that the fatty acids have been completely neutralised.

Example—

1 c.c. standard solution = 0·0284 grams stearic acid, and supposing that 50 c.c. were required to effect complete neutralisation of the fatty acids, then $50 \times 0{\cdot}0284 = 1{\cdot}420$ grams fatty acids in the sample, and the percentage will be $\frac{1{\cdot}420 \times 100}{5} = 28{\cdot}40$.

### (5) Degelatinised Bones.

According to the object the manufacturer has in view, they are wholly, or only partially, degelatinised. If the former, then they are solely used for manurial purposes; if the latter, they undergo carbonisation for animal charcoal.

(*aa*) *For artificial manures.*—Examination for nitrogen, as indicating the glue unextracted, and phosphates for the manurial value.

(*bb*) *For animal charcoal.*—The test is confined to organic matter, as a guide for the necessary carbon in the carbonised bone.

The analyses are made on the drawn samples dried at 100° to 105° C. for fourteen hours.

(*a*) *Nitrogen.*—This is determined by Keldjahl's method as described at (1) (*c*).

(*b*) *Phosphates.*—The method is described under "Manures."

(*c*) *Organic Matter.*—3 grams of the dried sample in a finely divided condition are weighed in a porcelain crucible, which must be of constant weight, placed in a muffle, and heated for twelve hours at a bright red heat; on removal of the crucible and cooling, the ash formed is moistened with a few drops of ammonium carbonate solution, dried in the air oven at 150° C. and weighed. The loss of weight represents the organic matter, the percentage being calculated according to the example.

Example—

| | |
|---|---|
| Crucible + sample, before ignition . . | 16·144 grams. |
| Crucible + ash, after ignition . . . | 15·700 ,, |
| Loss of weight (organic matter) . | ·444 ,, |

Then on the 3 grams taken the percentage is . . . . $\frac{\cdot 444 \times 100}{3} = 14{\cdot}80$ ,,

The calculation for ash is made on the weight of the crucible after ignition.

## (6) Animal Charcoal.

(*a*) *Moisture.*—This is made as described at (1) (*a*). The limit allowed is 8 per cent.

(*b*) *Carbon.*—The sample is finely pulverised, dried at 100° to 105° C. for several hours, and 2 grams weighed out for the analysis. It is treated with hydrochloric acid, and heated for one hour at 80° C., then filtered through a tared filter-paper, the residue and paper being well washed with hot

water until a portion of the filtrate gives no precipitate with nitrate of silver. Dry and reweigh. The increase of weight is the undissolved carbon and silicious matter. The filter-paper, with its contents, is now carefully folded into small bulk, placed in a crucible of constant weight, and ignited for twelve hours in a muffle at a bright red heat; the carbon by this means is burnt to carbonic acid, leaving as a residue the silica. Cool and reweigh.

Example—

| | |
|---|---|
| Filter-paper + residue (carbon and silica) | 1·213 grams. |
| Tare of filter-paper . . . | ·852 ,, |
| Residue . . . . | ·361 ,, |

Then on the 3 grams taken—

$\frac{\cdot 361 \times 100}{3} = 12\cdot 03$ per cent. of residual matter, carbon, and silica.

| | |
|---|---|
| Weight of crucible + silica + ash (filter-paper) after ignition . . . | 16·112 grams. |
| Tare of crucible . . . . | 16·062 ,, |
| | ·050 ,, |
| Less ash of filter-paper . . | ·003 ,, |
| Leaves silica . . | ·047 ,, |

The percentage calculation on the 3 grams taken is—

$\frac{\cdot 047 \times 100}{3} = 1\cdot 566$ as the yield of silica.

Then $12\cdot 03 - 1\cdot 566 = 10\cdot 464$ as the percentage of carbon in the charcoal.

### (7) Bone Superphosphates and Mixed Manures.

Under this heading, we shall refer to the principal special or finished manures, in which bone superphosphate forms the chief mixing ingredient, and also mineral phosphates and nitrogenous matters as admixtures in such manures.

As the manures are sold on the soluble and insoluble phosphates, potash, and ammonia they may contain, the work of the chemist is mainly devoted to estimating these constituents. We shall therefore confine ourselves to their separation and estimation.

*Sampling.*—In sampling from a heap of manure, great care should be taken in getting an average of the whole. For this purpose take eight or nine handfuls from the heap and mix well together on a sheet of paper, breaking down any lumps present. Then fill two 6-oz. bottles, which must be perfectly dry. One is used for analysis, and the other sealed and put away for future reference, if any dispute arise.

Raw materials, such as rock phosphates, etc., are ground to a powder, and then passed through a 60-mesh riddle, that portion retained by the riddle being again ground until fine enough to pass through the mesh.

(*a*) *Superphosphates.* — Superphosphates, as made from degelatinised bones, contain but very little nitrogen, which, if required, is determined by Keldjahl's method. The manure is valued on the soluble and insoluble phosphates it contains, and the determination is as follows:—A portion of the sample is ground in an agate mortar to a fine state of division, and 5 grams weighed. This is transferred to a porcelain mortar, and triturated with water, to dissolve the phosphate, the liquor then passed through a filter into a litre flask. The trituration is repeated some four times, and then the contents of the mortar washed on to the filter; wash the filter with cold water until the litre flask is about three parts full. On the filter is the insoluble, and in the filtrate the soluble phosphate. The flask is filled to the mark with cold water at 15·5° C., and 100 c.c. measured out (= ·5 gram of the sample); and in this is estimated the soluble phosphate, either by the citro-magnesic or molybdic method. Both give very accurate results with

careful manipulation. The writer, however, from his experience, prefers the former process. To prepare the ammonio-citrate of magnesia required, 270 grams citric acid are dissolved in hot water, and 27 grams carbonate of magnesia slowly added. The considerable effervescence produced, is due to the liberation of carbonic acid. The solution is further heated until the gas is driven off, then filtered into a litre flask, cooled, and 400 c.c. of a 10 per cent. solution of ammonia added, the whole being made to a litre at 15·5° C. with water. This forms the precipitating medium. The 100 c.c. containing the soluble phosphate are placed in a beaker, ammonia added until strongly alkaline, the precipitate of phosphate of lime formed being dissolved by the excess, and 60 c.c. of ammonio-citrate of magnesia added. The precipitate of ammonic-magnesic phosphate is slow at first in appearing, and is hastened by stirring for a few minutes. After standing for six to seven hours it is filtered, and then washed with a 2 per cent. solution of ammonia until the filtrate gives no precipitate with phosphate of soda. Dry, ignite, and weigh as magnesium pyrophosphate ($Mg_2P_2O_7$).

The calculation is as follows:—

| | | |
|---|---|---|
| Crucible + $Mg_2P_2O_7$ + ash (filter-paper) . . | 18·1490 | grams |
| Tare of crucible . . . | 18·0290 | ,, |
| | ·1200 | |
| Less ash . | ·0035 | ,, |
| Weight of $Mg_2P_2O_7$ found . | ·1165 | |

The factor for conversion of $Mg_2P_2O_7$ into tri-calcium phosphate ($Ca_3P_2O_8$) is 1·3964.

Then $·1165 \times 1·3964 = ·16268$ gram as the weight of tri-calcium phosphate in the 100 c.c. (·5 of the sample), or, in the 5 grams taken,

$·16268 \times 10 = 1·6268$ grams,

the percentage being $\frac{1·6268 \times 100}{5} = 32·536$.

(*b*) *Insoluble Phosphate.*—The residue on the filter, after washing out the soluble phosphate, is heated for half an hour with strong hydrochloric acid, and then evaporated to dryness on the sand bath, to render the silica insoluble. A few drops of strong hydrochloric acid are then added, shaken, then a little water, and the whole heated for a few minutes, and filtered. The filtrate containing the phosphate is made strongly alkaline with ammonia and the ammonio-citrate of magnesia added, the precipitate of ammonic-magnesic phosphate washed with a 2 per cent. solution of ammonia, dried, ignited, and weighed as magnesium pyrophosphate ($Mg_2P_2O_7$).

The calculation is the same as in soluble phosphate. In the molybdic method the solutions are precipitated with ammonium molybdate as yellow phosphate of molybdenum, then dissolved in dilute ammonia, and the phosphate precipitated with "magnesia mixture," as ammonic-magnesic phosphate, dried, ignited, and weighed as pyrophosphate ($Mg_2P_2O_7$); or the precipitate may be dissolved in a few drops of strong hydrochloric acid, and titrated in the usual way by a standard solution of uranic acetate.

It may here be remarked that all manures are sold on the basis of tri-calcium phosphate. Supposing, for instance, a manure contained 32 per cent. of soluble phosphate, calculated as tri-calcium phosphate, this would indicate that 32 per cent. of the original phosphate, either bone or mineral, had been made soluble by the treatment with sulphuric acid.

### (8) Special or Mixed Manures.

These manures are mixtures of superphosphates with varying proportions of nitrogen (either as organic nitrogen, nitrate of soda, or sulphate of ammonia) and potash.

(*a*) *Potash.*—The accurate estimation of potash in a manure is a very difficult operation, and requires great care

on the part of the chemist. The following method, and one which is adopted by leading agricultural chemists, yields very good results :—

Weigh out 5 grams, place in platinum basin with a little water, and to that add cream of lime (slaked lime made to a cream), and digest with heat. Pour off the liquor through a filter into a 250 c.c. flask, repeat the digestion twice, allowing to settle, then place the whole on to the filter, and wash up to the 250 c.c. mark. Take 50 c.c. ( = 1 gram of sample), run into small beaker, and precipitate with ammonium oxalate to get rid of the lime, then filter into a tared platinum dish, and evaporate down ; when nearly to dryness, add two or three drops sulphuric acid (sufficient to convert the whole into sulphates), then take to complete dryness, and ignite to drive off excess of sulphuric acid and ammonia salts. Weigh this, which represents sulphate of potash and sulphate of soda, in the sample. After weighing, dissolve in a little distilled water, and filter through a very small filter into a porcelain basin, then add two drops of hydrochloric acid and sufficient of platinic chloride (excess), and evaporate nearly to dryness, or to the thickness of a syrup, allow to stand half an hour, then wash by decantation two or three times with a little platinic chloride : this is done for the purpose of dissolving the soluble sodium platinic chloride ($Na_2PtCl_6$) ; the decanted washings are passed through a tared filter, and on this also is washed the residue left in the crucible. This residue is potassium platinic chloride ($K_2PtCl_6$). It is washed with alcohol to dissolve the excess of platinic chloride, and until no reaction for chlorine is seen in the filtrate, then slightly with special ammonium chloride solution, and finally with alcohol again ; dry at 100°, and weigh as $K_2PtCl_6$.

Example—

| | |
|---|---|
| Weight of filter-paper + $K_2PtCl_6$ . . | ·973 |
| Tare of filter-paper . . . | ·947 |
| Weight of $K_2PtCl_6$ found . . . | ·026 |

The factor for conversion of the $K_2PtCl_6$ into potash ($K_2O$) is ·193.

Then $·193 \times ·026 = ·05018$ as the corresponding weight of potash, and as 50 c.c. = 1 gram of the sample taken, the percentage = 5·018 ($K_2O$).

(*b*) *Soluble and insoluble phosphates* are found as in "Superphosphates" at (7) (*a*) and (*b*).

(*c*) *Nitrogen.*—If the nitrogen is of an organic nature, derived from added nitrogenous matter, then it is estimated by Keldjahl's method, as described. On the other hand, if its origin arises from nitrate of soda and sulphate of ammonia, the ammoniacal nitrogen of the latter is determined by distilling over the ammonia into a standard (decinormal) solution of sulphuric acid, and retitrating with decinormal soda solution, as described at (1) (*c*).

"Then," according to Griffith, "the contents of the flask, after distilling over the ammoniacal nitrogen, are treated, according to Siewert's method, with—

| | |
|---|---|
| 4 grams | iron filings. |
| 10 ,, | zinc powder. |
| 12 ,, | caustic soda. |
| 100 c.c. | alcohol (90 per cent. strength). |

"Allow the action to proceed as far as possible at the ordinary temperature, and then heat the flask gently. When all the alcohol has distilled over, run in 20 c.c. more, and distil. This operation of adding alcohol and distilling must be continued until moistened red litmus paper squeezed in between the cork and neck of the flask is not changed in colour. If the litmus turns blue, another 20 c.c. of alcohol

must be added to the flask and once more distilled, the nitric nitrogen passing over in the form of ammonia, and is absorbed as usual in a standard sulphuric acid."

The writer has made many determinations by this method, with very satisfactory results.

(*d*) *Moisture.*—The hydroscopical or mechanical moisture is determined by heating the sample to 100° C. for twelve hours. The water of combination requires a temperature of 145° to 150° C. before being driven off.

### (9) Mineral Phosphates.

Many classes of mineral phosphates come into the market, and some of these the manufacturer uses as an admixture with ground boiled bones for superphosphate making.

Their value depends on the tri-calcium phosphate they contain, and this is estimated by dissolving a finely ground sample in strong hydrochloric acid, and proceeding in the way as described under "Insoluble Phosphates."

### (10) Guanos.

Under this term are comprised a series of natural fertilisers, of which Peruvian guano may be considered the leading. Being a manure in themselves, they are used by the agriculturist unmixed with superphosphates. Their value depends on the phosphates and nitrogen they contain, the latter being in the form of ulmate, urate, chloride, and carbonate of ammonia. They are bought on a guarantee, and the works chemist is mainly called on to estimate the soluble and insoluble phosphate and nitrogen the guano contains.

(*a*) The nitrogen existing as ammonia is estimated by distilling 2 grams of the sample with milk of magnesia in a

flask connected with a Liebig's condenser, the volatile ammonia passed into a standard decinormal acid solution, and then retitrated with decinormal soda solution, as described. The total nitrogen, in the absence of nitrates, is determined by Keldjahl's method. If nitrates are present, the estimation is made according to the method given under "Special Manures" (8) (*c*).

(*b*) The phosphates, as soluble and insoluble, are determined by the processes described under "Superphosphates."

### (11) Dried Animal Products,

such as blood, flesh, hoofs, and horns, etc., are sometimes used in a crushed condition, by the manure-maker, for enriching manures with nitrogen. They are bought on the containing nitrogen, which is estimated in each case, on a finely divided sample, by Keldjahl's method. The organic matter, ash, and moisture are determined, if required, by the processes already described under their headings.

### (12) The Potash Compounds

used in the manure-shed are the muriate of potash and kainite, a mineral deposit obtained from Stassfurt, in Germany, and containing some 23 to 25 per cent. of sulphate of potash. The potash is determined by dissolving 35 grams either of the muriate or kainite in hot water, and filtering into a 500 c.c. flask, cooling, and making up to the mark at 15·5° C. Then measure out 10 c.c.( = ·7 gram of sample), and treat according to the method given under "Special Manures" (8) (*a*).

### (13) Sulphate of Ammonia

is the only ammoniacal salt used by the agriculturist. The ammonia is determined, as in guanos, in 2 grams of the

sample, by distillation with milk of magnesia, into a measured solution of decinormal acid, and then retitrated with decinormal soda, and from the resulting c.c., the ammonia and its equivalent as sulphate, calculated.

*Note.*—It may here be remarked that the methods described in the preceding pages are sufficient for all commercial purposes; the buyer requires no more, and neither does the seller; and, however interesting a full analysis may be from a scientific standpoint, the works chemist is but seldom called on to carry it out.

## TABLE OF ATOMIC WEIGHTS.

| Element. | Symbol. | Atomic Weight. | Element. | Symbol. | Atomic Weight. |
|---|---|---|---|---|---|
| Aluminium | Al | 27 | Nickel | Ni | 58·7 |
| Antimony | Sb | 119·9 | Niobium | Nb | 93·9 |
| Arsenic | As | 75 | Nitrogen | N | 14 |
| Barium | Ba | 137 | Osmium | Os | 195 |
| Bismuth | Bi | 208 | Oxygen | O | 16 |
| Boron | B | 10·9 | Palladium | Pd | 106 |
| Cadmium | Cd | 112 | Phosphorus | P | 31 |
| Cæsium | Cs | 133 | Platinum | Pt | 195·5 |
| Calcium | Ca | 40 | Potassium | K | 39·1 |
| Carbon | C | 12 | Rhodium | Rh | 104·3 |
| Cerium | Ce | 141·5 | Rubidium | Rb | 85·4 |
| Chlorine | Cl | 35·5 | Ruthenum | Ru | 103·8 |
| Chromium | Cr | 52 | Scandium | Sc | 44 |
| Cobalt | Co | 58·7 | Selenium | Se | 79 |
| Copper | Cu | 63 | Silicon | Si | 28 |
| Didymium | Di | 145 | Silver | Ag | 108 |
| Erbium | E | 166·4 | Sodium | Na | 23 |
| Fluorine | Fl | 19 | Strontium | Sr | 87·5 |
| Gallium | Ga | 70·1 | Sulphur | S | 32 |
| Glucinum | Gl | 9·1 | Tantalum | Ta | 182·7 |
| Gold | Au | 197 | Tellurium | Te | 128 |
| Hydrogen | H | 1 | Thallium | Tl | 204 |
| Indium | In | 113·7 | Thorium | Th | 232·5 |
| Iridium | Ir | 193 | Tin | Sn | 117 |
| Iron | Fe | 56 | Titanium | Ti | 48 |
| Lanthanum | La | 138·9 | Tungsten | W | 184 |
| Lead | Pb | 207 | Uranium | U | 240·5 |
| Lithium | Li | 7 | Ytterbium | Yb | 173 |
| Magnesium | Mg | 24 | Yttrium | Y | 89·8 |
| Manganese | Mn | 55 | Zinc | Zn | 65 |
| Mercury | Hg | 200 | Zirconium | Zr | 90·6 |
| Molybdenum | Mo | 96·2 | | | |

## TABLE OF THERMOMETRIC DEGREES.

| CENTIGRADE. | FAHRENHEIT. | REAUMUR. |
|---|---|---|
| Freezing 0° | Freezing 32° | Freezing 0° |
| 5° | 41° | 4° |
| 10° | 50° | 8° |
| 15° | 59° | 12° |
| 20° | 68° | 16° |
| 25° | 77° | 20° |
| 30° | 86° | 24° |
| 35° | 95° | 28° |
| 40° | 104° | 32° |
| 45° | 113° | 36° |
| 50° | 122° | 40° |
| 55° | 131° | 44° |
| 60° | 140° | 48° |
| 65° | 149° | 52° |
| 70° | 158° | 56° |
| 75° | 167° | 60° |
| 80° | 176° | 64° |
| 85° | 185° | 68° |
| 90° | 194° | 72° |
| 95° | 203° | 76° |
| Boiling 100° | Boiling 212° | Boiling 80° |

### RULES FOR CONVERSION.

Fahrenheit to Centigrade: $\frac{5(F-32)}{9} = C.$

Fahrenheit to Reaumur: $\frac{4(F-32)}{9} = R.$

Centigrade to Fahrenheit: $\frac{C \times 9}{5} + 32 = F.$

Centigrade to Reaumur: $\frac{C \times 4}{5} = R.$

Reaumur to Fahrenheit: $\frac{R \times 9}{4} + 32 = F.$

## COMPARISON BETWEEN THE BRITISH AND METRICAL SYSTEMS.

| | |
|---|---|
| 1 Pint. = ·5679 litre. | 1 Mile . = 1609·344 metres. |
| 1 Gal. . = 4·543 litres. | 1 Lb. . . = 453·6 grams. |
| 1 Inch. = ·0254 metre. | 1 Lb. (Troy) = 373·24 grams. |
| 1 Cb. in. = 16·38 cb. c'metres. | 1 Cwt. . = 50803·2 grams. |
| 1 Yard. = ·9144 metre. | 1 Ton . = 1,016,064 grams. |
| 1 Metre = 39·37079 inches. | 1 Kilogram . = 2·2046 lb. |
| 1 Litre = 1·76 pints. | 1 Kilometre . = 1093·611 yds |

| Conversion of | Multiplier. |
|---|---|
| Inches to metres | ·025399 |
| Metres to inches | 39·37079 |
| Square inches to square metres | ·0006451 |
| Square metres to square inches | 1550·6 |
| Cubic inches to cubic metres | ·0000163 |
| Cubic metres to cubic inches | 61027·05 |
| Gallons to litres | 4·543 |
| Litres to gallons | ·22009 |
| Pounds (avoirdupois) to grams | 453·592 |
| Grams to pounds (avoirdupois) | ·0022 |
| Pounds (Troy) to grams | 373·24 |
| Grams to pounds (Troy) | ·002679 |

## TABLE OF THE METRIC SYSTEM OF WEIGHTS AND MEASURES.

### LINEAR MEASURE.

10 Millimetres = 1 Centimetre.
10 Centimetres = 1 Decimetre.
10 Decimetres = 1 Metre.
10 Metres = 1 Dekametre.
10 Dekametres = 1 Hectometre.
10 Hectometres = 1 Kilometre.

The square and cubic measures are the square and cube of the linear measure respectively.

### MEASURES OF CAPACITY.

10 Millilitres = 1 Centilitre.
10 Centilitres = 1 Decilitre.
10 Decilitres = 1 Litre.
10 Litres = 1 Dekalitre.
10 Dekalitres = 1 Hectolitre.
10 Hectolitres = 1 Kilolitre.

### SYSTEM OF WEIGHTS.

10 Milligrams = 1 Centigram.
10 Centigrams = 1 Decigram.
10 Decigrams = 1 Gram.
10 Grams = 1 Dekagram.
10 Dekagrams = 1 Hectogram.
10 Hectograms = 1 Kilogram.

1 Litre = 1 Kilogram, or 1000 cubic centimetres.
1 Gram = 1 Cubic centimetre.

## TABLE OF FACTORS FOR DETERMINING THE EQUIVALENTS OF WEIGHED BODIES.

| FOUND. | WANTED. | FACTOR. |
|---|---|---|
| Alumina ($Al_2O_3$) | Sulphate of alumina ($Al_2(So_4)_3$) | |
| | Potash alum | |
| | Ammonia alum | |
| Barium sulphate ($BaSo_4$) | Barium oxide (BaO) | ·6569 |
| | Barium carbonate ($BaCo_3$) | ·8456 |
| | Sulphuric acid ($So_3$) | ·0343 |
| Magnesium pyrophosphate ($Mg_2P_2O_7$) | Phosphoric acid ($P_2O_5$) | ·6351 |
| | Tri-calcic phosphate ($Ca_3P_2O_8$) | 1·3964 |
| | Mono-calcic phosphate ($CaH_4P_2O_8$) | 1·0540 |
| | Bi-calcic phosphate ($Ca_2H_2P_2O_8$) | 1·2254 |
| | Magnesium sulphate ($MgSo_4$) | 1·0801 |
| | Magnesium chloride ($MgCl_2$) | ·8558 |
| | Magnesia (Mgo) | ·3606 |
| Potassic-platinic chloride ($K_2PtCl_6$) | Potash ($K_2O$) | ·1935 |
| | Potash chloride (KCl) | ·3062 |
| | Potassium sulphate ($K_2So_4$) | ·3579 |
| Lime (CaO) | Calcium sulphate ($CaSo_4$) | 2·4285 |
| Ammonia ($NH_3$) | Nitrogen (N) | ·8235 |
| | Ammonium sulphate, ($(NH_4)_2So_4$) | 7·7649 |
| Ferric oxide ($Fe_2O_3$) | Iron (Fe) | ·7000 |
| Carbonic acid ($Co_2$) | Calcium carbonate ($CaCo_3$) | 2·2727 |
| | Lime (CaO) | 1·2727 |
| Silver chloride (AgCl) | Chlorine (Cl) | ·2482 |
| | Sodium chloride (NaCl) | ·4092 |
| Lead sulphate ($PbSo_4$) | Lead oxide (PbO) | ·7359 |
| | Lead carbonate ($PbCo_3$) | ·8811 |
| | Lead (Pb) | ·6831 |
| Sodium sulphate | Sodium nitrate ($NaNo_3$) | ·5985 |
| | Sodium carbonate ($Na_2Co_3$) | ·7464 |
| | Sodium oxide ($Na_2O$) | ·4366 |

## TANKS AND CISTERNS.

### TO FIND THE CONTENTS—SQUARE OR OBLONG.

Reduce to inches, then multiply the length, width, and number of wet inches together for cubic inches, and convert the result into gallons by multiplying with ·003606 or dividing by 277·274.

For every foot deep, a tank having the dimensions of

| | | | | | |
|---|---|---|---|---|---|
| 4 | feet | × 4 | feet | holds 99·698 | gallons. |
| 5 | ,, | × 5 | ,, | 155·779 | ,, |
| 6 | ,, | × 6 | ,, | 224·322 | ,, |
| 7 | ,, | × 5 | ,, | 218·090 | ,, |
| 8 | ,, | × 6 | ,, | 299·096 | ,, |
| 9 | ,, | × 7 | ,, | 392·563 | ,, |
| 10 | ,, | × 8 | ,, | 498·493 | ,, |

### CIRCULAR.

Find the area of one end by multiplying the square of the diameter in inches by ·7854, then multiply by the depth.

For every foot deep a circular tank

| | | | | |
|---|---|---|---|---|
| 4 | feet in diameter | holds | 78·267 | gallons. |
| 5 | ,, | ,, | 122·348 | ,, |
| 6 | ,, | ,, | 184·936 | ,, |
| 7 | ,, | ,, | 239·804 | ,, |
| 8 | ,, | ,, | 276·314 | ,, |
| 9 | ,, | ,, | 328·192 | ,, |
| 10 | ,, | ,, | 384·286 | ,, |

---

The following data by Molesworth will enable a manufacturer to estimate the cost of any brickwork that may be required from time to time in his works:—

| Thickness of Wall. | For Cubic Yards. | For 1000 Bricks. |
|---|---|---|
| 1 brick | A × ·02778 | A × ·0106 |
| 1½ ,, | A × ·04167 | A × ·016 |
| 2 ,, | A × ·0555 | A × ·0213 |
| 2½ ,, | A × ·06944 | A × ·0267 |
| 3 ,, | A × ·08334 | A × ·032 |

A = the superficial area of wall in square feet. The number of bricks in a cubic yard = 384.

1 load of mortar = 1 cubic yard.

1 cubic yard of brickwork requires about . . . . . { 6½ cubic feet of sand. 2½ ,, of lime.

A wall, say, 20 feet × 10 feet and 2 bricks thick would require—4260 bricks; 72 cubic feet of sand; 28 cubic feet of lime.

---

Frequently the number of revolutions per minute is required of a wheel or pulley when driven by another of known diameter and revolutions per minute. The rule is to multiply the number of revolutions and known diameter together, and divide by the diameter of the wheel or pulley of which the number of revolutions is desired. For example—

Find the number of revolutions per minute made by a wheel 45 inches in diameter when driven by another 68 inches in diameter and making 62 revolutions.

$$\frac{68 \times 62}{45} = 93{\cdot}6,$$ the required number of revolutions.

# APPENDIX A.

## EVAPORATION IN VACUO.

### Description of a Vacuum Pan.

At the sea-level, with an atmospheric pressure of 760 millimetres, equal to 29·922 inches of mercury in the barometer, or, in other words, at a pressure of 15 lbs. on the square inch, water boils at a temperature of 212° F. (100° C.). If we ascend above this level, the layers of atmosphere become less dense and consequently exert less pressure, the boiling-point is reduced several degrees below 212° F. For instance, on the top of Ben Nevis (4400 feet high) water boils at 203·9° F. (95·5° C.), while at an altitude of 15,800 feet (the summit of Mont Blanc) it is lowered to 185·9° F. (85·5° C.).

With an increase of atmospheric pressure, as found in a deep mine, the reverse takes place, water requiring several degrees of heat above 212° F. before it actually boils.

If, then, we decrease the atmospheric pressure on the surface of a liquid, we lower the boiling-point of that liquid. On the other hand, if the pressure be increased above the normal, 760 millimetres, the boiling-point becomes proportionately higher, as seen from the following table:—

| | Pressure in lbs. per square inch. | Pressure in atmospheres. | Boiling-point. |
|---|---|---|---|
| Below the normal pressure. | ... | 0·180 | 32·0° F. |
| | 3 | 0·210 | 140·0° F. |
| | 9 | 0·610 | 186·8° F. |
| Normal pressure at the sea-level. | 15 | 1·020 | 212·0° F. (Boiling-point normal.) |
| Above the normal pressure. | 22 | 1·500 | 234·5° F. |
| | 30 | 2·040 | 250·5° F. |
| | 45 | 3·060 | 275·7° F. |

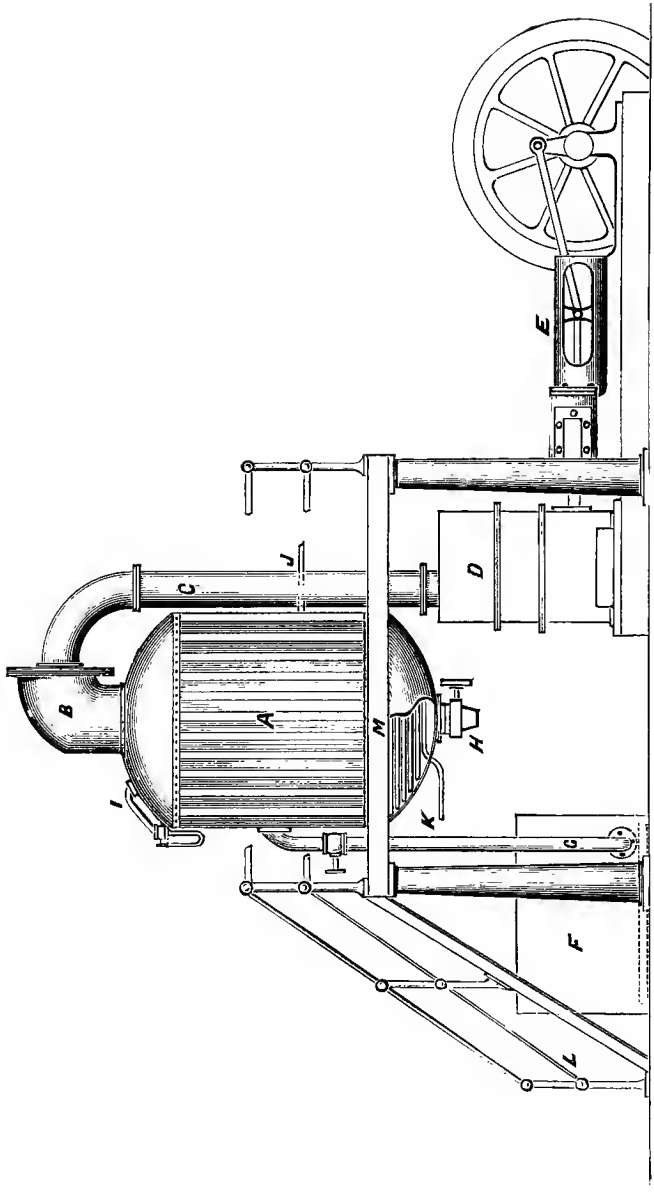



FIG. 17.—Vacuum Pan.

This variation of the boiling-point of water with pressure has been turned to advantage in many manufacturing processes by the introduction of the vacuum pan, whereby under a reduced pressure, produced by mechanical means, liquors can be concentrated without injury to the active principle they contain. By working under a low pressure, clarified sugar juices, food extracts, glycerine, dyewood, gelatine, and other liquors can be concentrated to any desired extent without injury, whereas exposure to a temperature of boiling water for any prolonged period, as evaporating in an open pan, their constitution would to a more or less extent undergo a prejudicial change. In 1813, Howard constructed the first vacuum pan, and since that time great improvements have been made in adapting it to modern requirements.

The pans now in use are built of wrought-iron, steel, or copper, and in form are either cylindrical or nearly spheroidal. The latter shape finds favour in sugar refineries, and is made of two nearly semi-globular portions united at the centre by outside flanges. At the top is fixed the dome fitted with baffle-plates, and to which is connected the condenser and vacuum pump. At the bottom is placed the discharge valve for emptying the pan of its contents. The heating is carried out by internal circular pipes, or by a steam jacket round the lower half of the pan. The cylindrical form, built of wrought-iron or steel plates, is used for evaporative purposes in many processes, and also in this shape are the pans of the double, triple, and quadruple effects, as noticed further on.

In Fig. 17 is seen an elevation of a vacuum pan for evaporating glue and gelatine liquors. The pan is built of steel plates, and lined outside with woodwork, and rests on a floor constructed of rolled steel plates, supported on four columns, with a stairway leading to the working platform. One-half of the lower part is shown in section, giving a view of the coils by which the pan is heated. The various parts are as follows:—

*A*. The body of the pan.
*B*. The dome.

*C.* Exhaust pipe leading from dome to condenser.
*D.* Condenser.
*E.* Air or vacuum pump.
*F.* Storage tank for glue or gelatine liquors, warmed with steam coil.
*G.* Supply pipe leading from storage tank to vacuum pan.
*H.* Discharge valve.
*I.* Barometer gauge for indicating vacuum.
*J.* Inlet steam pipe for supplying the coils.
*K.* Exhaust end of vacuum coils.
*L.* Iron staircase.
*M.* Steel floor.

The accessories to the pan are placed in a convenient position above the working floor, and include a steam gauge for noting the pressure in the coils, a gauge for indicating the height of the liquor in the pan, vacuum gauge *I*, as shown in the drawing, air-cocks and a thermometer. The pan is also fitted with a small apparatus, by which portions of the boiling liquor can be drawn from time to time, without disarranging the vacuum, so that the progress of evaporation can be ascertained.

In working the pan, the storage tank *F* is first filled with the weak glue liquors to be evaporated; the valve on the supply pipe *G* is then closed, and the vacuum pump set in motion; a few strokes are sufficient to reduce the internal pressure, and the valve of the supply pipe is then opened, and the liquor allowed to fill up the pan to the desired mark on the gauge. The valve is then closed, and the steam inlet valve *J*, supplying the coils, opened. As the heat from the coils spreads through the liquor, the vacuum pump is kept steadily at work reducing the inside pressure to within 2 to $2\frac{1}{2}$ inches of a perfect vacuum, as seen on the barometrical scale. In this vacuum the liquor will boil at 120° to 130° F., and the boiling is continued until the withdrawn samples, as tested by the glue-meter, show the desired strength. The pump is then stopped, the vacuum broken by opening the air-cocks, and the concentrated liquor is run through the valve *H* into suitably arranged receiving tanks, for supplying the trays or glasses for jellying.

For economical working with large quantities of weak liquors, a combination of two, three, and even four vacuum pans, forming the double, triple, and quadruple effect evaporators, have been designed for concentration purposes. The triple effect is, however, the system mostly in use, and consists of a grouping of three cylindrical pans, each connected by suitably arranged piping, by which the vapours of the first pan are conveyed to and made to heat the coils of a second pan, the resulting vapours from the second, passing on to a third pan, for a similar purpose. All the pans are connected with powerful pumps, producing a nearly absolute vacuum in each. The liquor is evaporated to a given density in the first pan, and then passed on to the second, and ultimately to the third, at which stage 80 per cent. of its water will have been driven off.

# APPENDIX B.

## GELATINE.

### Comparison between French and British Gelatines.

The following is a comparison of the yields of British and French makers of Gelatine, confined to the ash and water absorption, the latter indicating the economical value. The water absorption is based on grams.

| Brand. | Ash. | Water absorption by 28·34 grams. of substance taken. |
|---|---|---|
| | | Grams. |
| Coignet's Gold Label Gelatine . | 1 per cent. | 340·08 |
| Coignet's Special . . . | 1 „ | 340·08 |
| Nelson's No. 1 Photographic Gelatine . . . . | 2 „ | 283·4 |
| Ordinary French, not branded . | 2 „ | 292·81 |
| Cox's Gelatine in Packets . | 1 „ | 279·62 |

Undoubtedly, the French superiority in the production of Gelatines rests on the great care exercised in selection, and the close scientific supervision of every operation. The crystal White Leaf Gelatine is made from a careful assortment of the cuttings of prepared skins used in the manufacture of white kid gloves. Such a product realises £190 to £200 per ton.

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